



# Ab Initio Stopping Power Simulations for Ions with Electrons in Matter

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# *Ab Initio* Stopping Power Simulations for Ions with Electrons in Matter

*Simulations ab initio du pouvoir d'arrêt pour les ions  
contenant des électrons dans les matières*

## Thèse de doctorat de l'université Paris-Saclay

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**Titre :** Simulations *ab initio* du pouvoir d'arrêt pour les ions contenant des électrons dans les matières  
**Mots clés :** TDDFT en temps réel, Pouvoir d'arrêt électronique, Base localisée du type gaussienne, Déplacement de la base du projectile, Systèmes atomiques et métalliques

**Résumé :** La consommation de combustibles fossiles est un facteur principal des émissions de gaz à effet de serre. Face à une crise climatique planétaire, des solutions énergétiques alternatives s'imposent. L'énergie nucléaire présente l'avantage de la production de masse, mais expose les matériaux de structure à un environnement extrême dont les dommages doivent être étudiés. Les expériences traditionnelles utilisant des faisceaux de neutrons sont souvent coûteuses avec des échantillons difficiles à manipuler. Une meilleure alternative est l'irradiation aux ions.

Une quantité importante mesurée lors de l'irradiation aux ions est le pouvoir d'arrêt, dont la référence la plus standard est le SRIM. Cette méthode empirique de calculs est ajustée sur une base de données expérimentales très complète. Mais pour les irradiations peu documentées, la fiabilité du SRIM n'est pas garantie et les calculs *ab initio* peuvent servir de références supplémentaires. Implémentée au sein du code MOLGW, notre méthode de simulation s'appuie sur la théorie de la fonctionnelle de la densité dépendante du temps (TDDFT). L'utilisation de fonctions de base localisées du type gaussienne permet de décrire tous les électrons. L'objectif de cette thèse est d'introduire des fonctions de bases localisées suivant le projectile pour prendre en compte de ses électrons.

Puisque la base du projectile se déplace, les équations de Schrödinger dépendantes du temps doivent être modifiées. On constate notamment l'apparition d'un opérateur  $\hat{D}$  indispensable à la conservation d'orthonormalité de fonction d'onde. Cet opérateur contribue à une énergie  $E_{-iD}$  dont la précision numérique dépend fortement de la qualité de base. Le propagateur de Crank-Nicolson est choisi à la place du propagateur de Magnus du second ordre, en raison du fait que ce premier nécessite moins d'approximations dans une base non-orthogonale. Une stratégie de prédiction-correction est appliquée à la propagation.

La mise à jour de matrices de grande taille demande beaucoup d'efforts de calcul pendant la propagation. Afin de réduire le coût, seuls les termes croisés entre la cible et le projectile sont sélectionnés pour le recalcul. L'implémentation a été validée par des tests de collisions atomiques avant d'être appliquée aux cibles solides. Notre approche traite les systèmes finis et les structures cristallines sont décrits par les agrégats. Deux groupes de paramètres de modélisation sont vérifiés par rapport à la convergence : la géométrie de l'agrégat et la qualité de base. On conseille un agrégat de forme cylindrique fin et long pour assurer la stationnarité du transfert d'énergie. Quant à la base, les séries cc-pCVXZ de Dunning sont les plus adaptées pour les atomes de cible ainsi que pour les projectiles possédant d'électrons de coeur. Pour les projectiles plus légers, les séries standard cc-pVXZ suffisent. Les pouvoirs d'arrêt canalisés le long des directions cristallines (channeling en anglais) d'hydrogène et d'hélium sont étudiés dans un agrégat d'aluminium fcc [001]. Les résultats du channeling convergent plus rapidement quand l'agrégat est centré sur le canal.

Les pouvoirs d'arrêt moyennés (random en anglais) d'hydrogène et d'hélium dans le lithium et l'aluminium sont analysés, ainsi que celui d'aluminium dans l'aluminium. Malgré un léger manque de convergence, nos résultats sont qualitativement corrects et en bon accord avec le SRIM, les données expérimentales et les résultats obtenus en base d'ondes planes par un autre groupe. Enfin une étude en parallèle de pouvoirs d'arrêt de proton et d'antiproton dans le LiF calculés sans la base de projectile sont montrés. Nos simulations décrivent correctement les comportements du pouvoir d'arrêt de proton observés par les expériences. En outre, on prédit un effet de Barkas négatif sans précédent à très basse vitesse. On explique cet effet par la déstabilisation d'une orbitale  $2p$  d'ion  $F^-$  par un antiproton proche.

**Title :** *Ab Initio* Stopping Power Simulations for Ions with Electrons in Matter

**Keywords :** Real-time TDDFT, Electronic stopping power, Localized GTO basis, Projectile basis movement, Atomic and metallic systems

**Abstract :** The burning of fossil fuels is the major culprit of greenhouse gases emission contributing to the global climate crisis. Among many alternative energy solutions, the nuclear power stands out for its capacity in massive production. However, the intense nuclear reactions create a detrimental environment for reactor materials. To understand the material damages caused by radiations, experiments traditionally use neutron beams. These experimental settings are often expensive with samples difficult to manipulate. These disadvantages are the reasons why the use of ion beams becomes a popular alternative.

One key parameter for the ion irradiation is the electronic stopping power, whose value is usually obtained from the SRIM code. This empirical method is based on a very complete database. However, it may lose its reliability when the irradiated systems have hardly any experimental records in the database. Calculations from first-principles thus provide supplementary references to experiments. Implemented inside the MOLGW code, our simulation method for the electronic stopping power is based on the time-dependent density functional theory (TDDFT). Using localized Gaussian-type orbital basis functions, our code can describe all the electrons, core and valence. The main goal of this thesis is to incorporate basis functions following the movement of the projectile and simulate the irradiation of ions containing electrons.

Modifications to the time-dependent equations, notably the appearance of an operator  $\hat{D}$ , are necessary due to the movement of projectile basis. This extra operator enforces the conservation of the wave-function orthonormality and has an energy contribution  $E_{-iD}$  whose numerical precision depends on the basis set completeness. The Crank-Nicolson propagator is chosen over the second-order Magnus propagator due to less approximations required in the non-orthogonal basis. A predictor-corrector scheme is applied to evaluate the propagated states.

In order to reduce the computational costs of large matrix updates during the propagation, only the cross target-projectile elements are selected for recalculations. The sanity of our implementations is verified by tests in atomic systems before applying the code to solid targets. Since our approach works with finite systems, the infinite crystal structure is represented by a cluster. Two main groups of modeling parameters vital to the convergence are studied : the cluster geometry and the basis set quality. We advocate for the use of a long and thin cylindrical shape for the clusters to guarantee the stabilization of the energy transfer between the projectile and the target. High quality cc-pCVXZ Dunning basis are needed for target atoms and projectiles with core electrons. For lighter projectiles the standard cc-pVDZ basis is sufficient. The channeling stopping powers of hydrogen and helium are studied in fcc [001] aluminum target and converge faster when the cluster is centered on its channel rather than on its central column of atoms.

The random electronic stopping powers of hydrogen and helium in lithium and aluminum are presented, as well as the results for aluminum ion in aluminum. Our calculations, although not fully converged, provide accurate qualitative insights of the stopping power behaviors in good general agreement with the SRIM prediction, the experimental data and the results obtained with plane-wave basis method from another group. We also report the random stopping powers of proton and antiproton in LiF calculated without projectile basis from a side project. Our results describe correctly the proton stopping power observed by experiments like the threshold velocity and the Barkas effect where the stopping power of antiproton is inferior to that of proton. Additionally, we have observed an unprecedented negative Barkas effect at very low velocities due to the destabilization of the  $2p$  orbitals of  $F^-$  ions in the presence of a close antiproton.



# Résumé en français

La consommation de combustibles fossiles est un facteur principal des émissions de gaz à effet de serre. Face à une crise climatique planétaire, des solutions énergétiques alternatives s'imposent. L'énergie nucléaire avec sa capacité de production de masse est souvent considérée comme une solution de choix [1]. En même temps, les réactions nucléaires au sein du réacteur créent un environnement extrême pour les matériaux de structure dont les dommages doivent être vigoureusement étudiés. Étant l'acteur principale d'endommagement nucléaire [2], les neutrons sont souvent utilisés dans les expériences d'irradiation des matériaux. Cependant, les ions sont devenus une alternative populaire aux neutrons grâce à la facilité de contrôle de conditions expérimentales, le coût avantageux d'installation et la rapidité d'irradiation [3]. Le sujet de cette thèse est donc inspiré par les études d'endommagement de matériaux sous irradiation ionique effectuées au sein du Commissariat à l'Énergie Atomique et aux Énergies Alternatives (CEA) à Saclay.

Une quantité importante mesurée lors de l'irradiation aux ions est le pouvoir d'arrêt, qui est défini comme la perte de l'énergie cinétique du projectile divisée par la distance qu'il traverse [4]

$$S(v) = -\frac{dE_{kin}^{proj}(v)}{dx}. \quad (1)$$

Cette quantité dépend de la vitesse du projectile et peut être séparée en deux parties : le pouvoir d'arrêt nucléaire et le pouvoir d'arrêt électronique [5]. D'un côté, la partie nucléaire est régie par la mécanique classique, mais de l'autre la partie électronique ne peut qu'être traitée en mécanique quantique. Puisque le pouvoir d'arrêt nucléaire devient négligeable dans la gamme d'énergie cinétique qui nous intéresse, l'effort de cette thèse se concentre uniquement sur la partie électronique qui résulte d'excitations et ionisations des électrons dans le matériau cible.

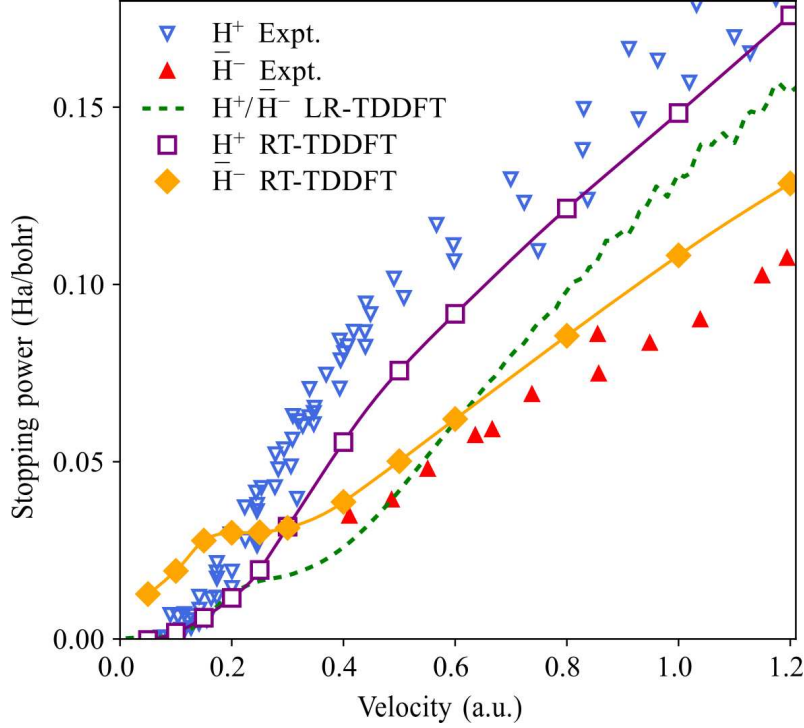
Les mesures expérimentales de pouvoir d'arrêt sont souvent comparées aux références numériques dont la plus standard est le code SRIM (the Stopping and Range of Ions in Matter en anglais) [6]. Cette méthode de calculs empirique est ajustée sur une grande base de données expérimentales avec des règles d'ajustement particulières [7]. Il y a plusieurs limitations dans SRIM dont une est la grande barre d'erreur parmi les données expérimentales. Un autre désavantage de SRIM est que si les irradiations du système étudié sont peu documentées la fiabilité de la prédiction du SRIM n'est plus garantie. Pour ces

raisons, les calculs *ab initio* sont demandés afin de servir de références supplémentaires. Implémentée au sein du code MOLGW [8], notre méthode de simulation s'appuie sur la théorie de la fonctionnelle de la densité (DFT) pour calculer les états stationnaires du système initial et la DFT dépendante du temps (TDDFT) pour les états excités. Ce dernier nous amène à résoudre l'équation de Schrödinger dépendante du temps

$$i\frac{\partial}{\partial t}\Psi(t) = \hat{H}(t)\Psi(t). \quad (2)$$

L'utilisation de fonctions de base localisées du type gaussienne permet de décrire tous les électrons sans pseudo-potentiel. En pratique dans les simulations numériques, il est courant de donner une vitesse constante au projectile et mesurer l'accroissement de l'énergie totale du système au lieu de mesurer la perte d'énergie cinétique du projectile dans une dynamique Newtonienne. Ces deux approches sont équivalentes mais la première est plus simple à mettre en place [9].

Puisque le travail de cette thèse est une continuation de la thèse précédente d'Ivan Maliyov [10] avec Fabien Bruneval et Jean-Paul Crocombette, la première partie du manuscrit est dédiée à résumer les développements précédents de simulations de TDDFT en temps réel (RT) de l'irradiation ionique avec des bases sur les atomes fixes. Un nouveau cas d'application de ce développement est réalisé durant cette thèse où l'on a calculé les pouvoirs d'arrêt du proton et de l'antiproton dans l'isolant LiF [11]. Une particularité de pouvoir d'arrêt dans un isolant est que, à cause de la bande d'énergie interdite, le pouvoir d'arrêt électronique d'un projectile est nul si l'énergie cinétique du projectile n'est pas suffisante pour franchir la bande interdite. Ce seuil d'énergie n'est pas présent si le projectile traverse un métal. Comme démontré en Figure 1, nos simulations de RT-TDDFT décrivent correctement, par rapport aux expériences, le seuil du pouvoir d'arrêt du proton ainsi que l'effet de Barkas [12] où le pouvoir d'arrêt du proton devient plus grand que celui de l'antiproton. En outre, on prédit une absence de seuil pour l'antiproton et un effet de Barkas négatif à très basse énergie cinétique où le pouvoir d'arrêt de l'antiproton dépasse celui du proton. On explique ce phénomène par la déstabilisation d'orbitales  $2p$  d'ion  $F^-$  en présence d'un antiproton proche.



**FIGURE 1** – Le pouvoir d’arrêt (stopping power) du proton et de l’antiproton dans LiF aux différentes vitesses (velocity). Les triangles bleus et rouges représentent les données expérimentales [13, 14, 15] pour le proton et l’antiproton respectivement. La ligne verte brisée trace les résultats de calculs du TDDFT en réponse linéaire (LR-TDDFT) qui est une méthode insensible à la signe du charge de projectile. Nos résultats de calculs du RT-TDDFT [11] sont représentés par les lignes avec diamants : la couleur violette est utilisée pour les résultats du proton et la couleur orange pour l’antiproton.

Le nouveau développement au centre de cette thèse est l’introduction de fonctions de bases qui suivent le projectile. La motivation derrière ce travail est l’inadaptation du développement précédent dans les cas de projectiles possédant des électrons. Puisque les fonctions de base du projectile se déplacent, la solution de l’équation de Schrödinger dépendante du temps doit être modifiée. Notamment l’opérateur de la dérivée du temps dans l’équation (2) se transforme en [16]

$$\frac{\partial}{\partial t} \Rightarrow \frac{d}{dt} = \frac{\partial}{\partial t} + \sum_{A=1}^N \frac{\partial \mathbf{R}_A}{\partial t} \cdot \nabla_{\mathbf{R}_A}. \quad (3)$$

On constate en conséquence l’apparition d’un opérateur  $\hat{D}$  qui décrit la variation temporelle de la base et est indispensable à la conservation d’orthonormalité de fonction d’onde [16, 17].

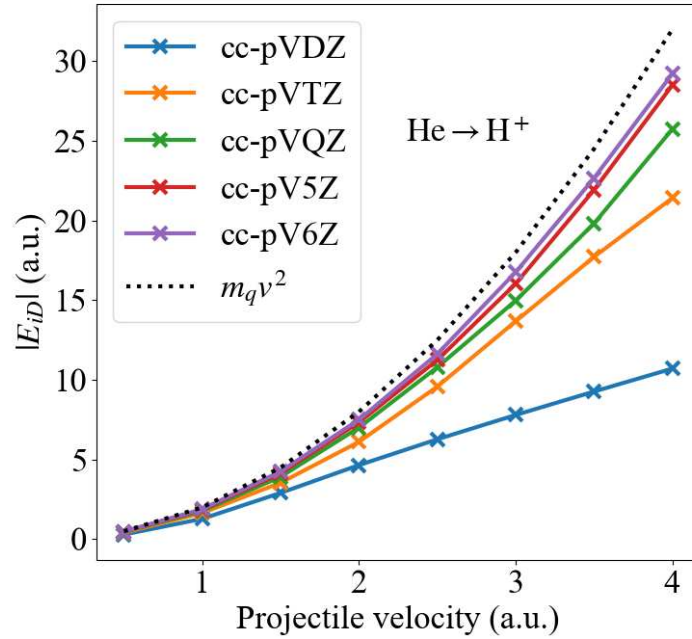
En cas de la vitesse constante du projectile, l'opérateur  $\hat{D}$  devient

$$\hat{D} = \sum_{A=1}^N \frac{\partial \mathbf{R}_A}{\partial t} \cdot \nabla_{\mathbf{R}_A} = \sum_{A=1}^N \mathbf{v}_A \cdot \nabla_{\mathbf{R}_A} \quad (4)$$

où  $\mathbf{R}_A$  désigne la position de l'atome  $A$  du système et  $N$  le nombre total d'atomes. Cet opérateur correspond à une énergie

$$E_{-iD} = -m_q \mathbf{v}^2 \quad (5)$$

dont la précision numérique dépend fortement de la qualité de base et diminue lorsque la vitesse du projectile s'élève, comme indiqué par Figure 2. Le propagateur de Crank-Nicolson a été retenu. Une stratégie de prédiction-correction est appliquée à la propagation pour améliorer l'évaluation de l'opérateur hamiltonien dépendant du temps [18].



**FIGURE 2** – L'approximation de l'énergie  $E_{-iD}$  à la valeur théorique  $m_q v^2$  pour un atome d'hélium allant vers un proton aux plusieurs vitesses (projectile velocity). La qualité de base (série de Dunning [19]) est la même pour tous les deux particules. La valeur absolue de  $E_{-iD}$  est tracée par la ligne pleine en différentes couleurs pour les bases de qualités différentes, de la plus basse cc-pVDZ à la plus haute cc-pV6Z. La ligne noire pointillée représente la valeur théorique de  $m_q v^2$ .

A cause de la dépendance en temps, les intégrales contenant les fonctions de bases qui se déplacent doivent être mises à jour à chaque pas de temps, ce qui consomme beaucoup d'efforts de calcul. Afin de réduire ce coût, seuls les termes croisés entre la cible et le

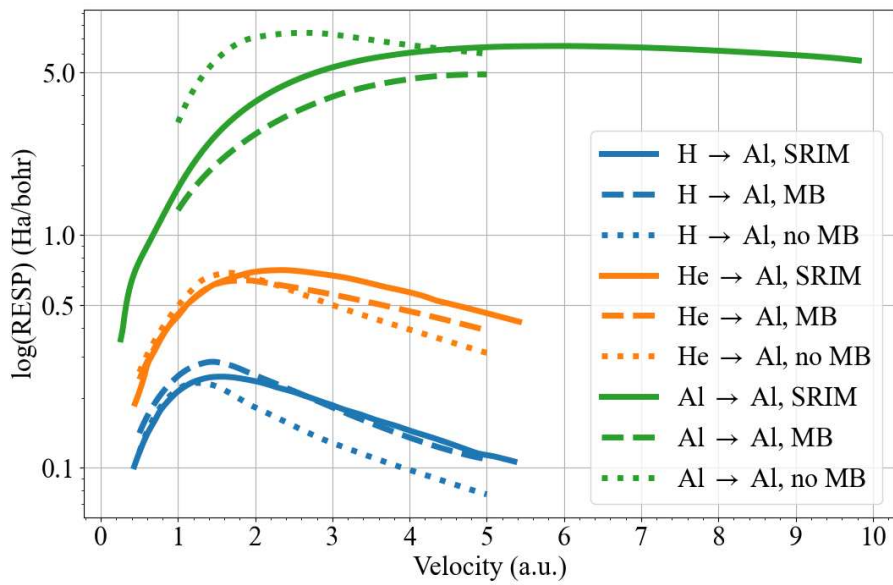
projectile sont sélectionnés pour la mise à jour puisque les termes purement cible ou projectile sont invariants dans le temps. La nouvelle implémentation avec les fonctions de base mobiles a été validée par des tests de cibles atomiques avant d'être appliquée aux cibles solides. Le plus instructif de ces tests est de vérifier que la gain d'énergie totale soit le même quand on inverse les rôles de cible et projectile dans un système diatomique.

Avec les fonctions de base localisées, on travaille dans les systèmes finis et les structures cristallines sont décrites par les agrégats. Deux groupes de paramètres de modélisation sont inspectés par rapport à la convergence avec les fonctions de base mobiles : la géométrie de l'agrégat et la qualité de base. On trouve qu'un agrégat de forme cylindrique fin et long peut assurer la stationnarité du transfert d'énergie après la phase de transition entre les calculs des états stationnaires et les calculs dépendants du temps. Quant à la qualité de base, les séries de base de Dunning [19, 20, 21] sont étudiées. On observe que les séries cc-pCVXZ sont les plus adaptées pour les atomes de cible ainsi que les projectiles possédant d'électrons de cœur. Pour les projectiles plus légers, les séries standards cc-pVXZ suffisent. Il y a une tendance générale que plus la qualité de base du cible est bonne, plus le pouvoir d'arrêt est élevé. Cependant, cette conclusion n'est plus vraie pour la qualité de la base sur le projectile. On constate qu'il faut améliorer en même temps la base du cible et du projectile afin d'obtenir la convergence.

Le premier solide étudié est le métal lithium, choisi pour la simplicité de sa configuration électronique. Le pouvoir d'arrêt de l'hydrogène dans lithium obtenu avec les fonctions de base mobiles est en bon accord avec les données expérimentales ainsi qu'avec les résultats de calculs à la base fixe. Le pouvoir d'arrêt de l'hélium est plus difficile à interpréter car il n'existe qu'une seule donnée expérimentale et que les résultats de la base mobile se comportent différemment à la fois de la prédiction de SRIM et des résultats de la base fixe. Les effets de taille d'agrégat, de qualité de base et de discrétisation temporelle sont étudiés, mais cet écart de comportements persiste et demanderait des études complémentaires.

Un autre solide étudié est le métal aluminium dans lequel les pouvoirs d'arrêt de l'hydrogène et de l'hélium sont calculés. Ces résultats de la base mobile sont en accord non seulement avec les expériences mais aussi avec les études en onde plane de Schleife et ses collègues [22]. En même temps, les résultats de la base mobile ainsi que ceux de Schleife ont tous sous-estimé les pouvoirs d'arrêt aux hautes énergies cinétiques. Cette sous-estimation était déjà observée dans les simulations *ab initio* antérieures et des études

précédentes [23, 24] ont tenté de corriger en améliorant la description d'électrons de coeur, la qualité de base et en changeant les fonctionnelles d'échange et corrélation sans trouver des solutions. On a également utilisé l'aluminium comme projectile dans le cible aluminium afin de simuler un projectile possédant d'électrons de coeur. Les résultats de la base mobile montrent un comportement en bon accord avec SRIM et les données expérimentales, malgré une légère sous-estimation. Figure 3 résume pour les trois projectiles étudiés dans la cible aluminium et on remarque de visibles améliorations qualitative et quantitative apportées par la base mobile en comparaison avec les résultats de la base fixe.



**FIGURE 3** – Les pouvoirs d'arrêt randoms (RESP) en échelle log de trois projectiles étudiés dans l'aluminium aux différentes vitesses (velocity) : hydrogène (représenté par la couleur bleu), hélium (orange) et aluminium (vert). Predictions du code SRIM [6] sont tracées avec de lignes pleines. Les résultats calculés avec les fonctions de base sur le projectile (MB) sont tracés avec de lignes brisées et les résultats obtenus sans les fonctions de base de projectile (no MB) sont tracés avec de lignes pointillées.

En conclusion, une partie de cette thèse est consacrée à l'étude de pouvoirs d'arrêt du proton et de l'antiproton dans LiF en appliquant l'ancien développement avec la base fixe. Un effet de Barkas négatif sans précédent y est observé. La majorité de cette thèse porte sur le nouveau développement avec la base mobile afin de décrire les électrons de projectile. Des améliorations remarquables sont obtenues par rapport aux simulations avec la base fixe. Notre code actuel est optimisé et le calcul d'une trajectoire dans le solide se termine sous 24h avec moins de 300 cœurs sur les machines de calculs du Tier 1, tandis que d'autres études similaires demandent presque 1 million de cœurs [25]. Afin de rendre les résultats

de cette thèse plus robustes, il est indispensable d'améliorer la convergence en utilisant des bases plus complètes et mieux adaptées. Il sera utile de collaborer avec les équipes expérimentatrices dans les cas où les données expérimentales sont manquantes. Enfin, nous ambitionnons de pouvoir appliquer le développement de cette thèse sur des projectiles plus lourds dont les pouvoirs d'arrêt sont mal prédits par le SRIM, comme l'or dans SiC [26].



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# Abbreviations

|                    |                                                                          |
|--------------------|--------------------------------------------------------------------------|
| <b>CSDA</b>        | Continuous Slowing Down Approximation                                    |
| <b>BSE</b>         | Basis Set Exchange                                                       |
| <b>GTO</b>         | Gaussian Type Orbitals                                                   |
| <b>DFT</b>         | Density Functional Theory                                                |
| <b>TDDFT</b>       | Time-Dependent Density Functional Theory                                 |
| <b>RT-TDDFT</b>    | Real-Time Time-Dependent Density Functional Theory                       |
| <b>LR-TDDFT</b>    | Linear-Response Time-Dependent Density Functional Theory                 |
| <b>TDSE</b>        | Time-Dependent Schrödinger's Equation                                    |
| <b>TDKS</b>        | Time-Dependent Kohn and Sham                                             |
| <b>ETF</b>         | Electron Translation Factor                                              |
| <b>SCF</b>         | Self-Consistent Field                                                    |
| <b>MAG2</b>        | Second-order MAGnus (propagator)                                         |
| <b>CN</b>          | Crank-Nicolson (propagator)                                              |
| <b>SP</b>          | Stopping Power                                                           |
| <b>RESP</b>        | Random Electronic Stopping Power                                         |
| <b>cc-pVXZ</b>     | correlation-consistent polarized Valence $X$ -Zeta (basis set)           |
| <b>aug-cc-pVXZ</b> | augmented correlation-consistent polarized Valence $X$ -Zeta (basis set) |
| <b>cc-pCVXZ</b>    | correlation-consistent polarized Core-Valence $X$ -Zeta (basis set)      |
| <b>MB</b>          | Moving (projectile) Basis                                                |

---

# Mathematical Symbols

## Operators

|           |                                      |
|-----------|--------------------------------------|
| $\hat{H}$ | Hamiltonian operator                 |
| $\hat{T}$ | Kinetic operator                     |
| $\hat{W}$ | Electron-electron potential operator |
| $\hat{V}$ | External potential operator          |
| $\hat{D}$ | Time derivative operator             |
| $\hat{M}$ | Effective Hamiltonian operator       |

## Matrices

|                      |                                       |
|----------------------|---------------------------------------|
| $C$                  | Coefficient matrix of basis functions |
| $D$                  | Time derivative matrix                |
| $H$                  | Hamiltonian matrix                    |
| $V$                  | External potential matrix             |
| $V_H$                | Hartree potential matrix              |
| $V_{xc}$             | Exchange-correlation matrix           |
| $E$                  | Energy matrix of the Hamiltonian      |
| $S$                  | Overlap matrix                        |
| $P$                  | Density matrix                        |
| $\mathbf{L}$         | Left gradient of overlap matrix       |
| $\mathbf{v}_{basis}$ | Velocity matrix of basis centers      |

## Others

|           |                                     |
|-----------|-------------------------------------|
| $N_{BF}$  | Number of basis functions           |
| $N_{ABF}$ | Number of auxiliary basis functions |
| $N_{OCC}$ | Number of occupied states           |



# Contents

|          |                                                                  |           |
|----------|------------------------------------------------------------------|-----------|
| <b>1</b> | <b>Introduction</b>                                              | <b>1</b>  |
| 1.1      | Research Inspirations . . . . .                                  | 1         |
| 1.1.1    | Experiments . . . . .                                            | 3         |
| 1.1.2    | Applications . . . . .                                           | 4         |
| 1.2      | Electronic Stopping Power . . . . .                              | 5         |
| 1.2.1    | Definition . . . . .                                             | 5         |
| 1.2.2    | Early analytical models . . . . .                                | 6         |
| 1.3      | Simulation Program MOLGW . . . . .                               | 7         |
| <b>2</b> | <b>Fundamental Theories and Technical Background</b>             | <b>9</b>  |
| 2.1      | From Stationary to Time-Dependent DFT . . . . .                  | 9         |
| 2.2      | Choice of Basis Sets . . . . .                                   | 12        |
| 2.2.1    | Mixed Dunning basis technique . . . . .                          | 13        |
| 2.2.2    | Matrix representations in localized basis sets . . . . .         | 15        |
| 2.2.3    | 4-center integrals approximations . . . . .                      | 17        |
| 2.3      | Systems Without Projectile Basis . . . . .                       | 19        |
| 2.3.1    | Canonical orthogonalization . . . . .                            | 20        |
| 2.3.2    | Real-time propagation . . . . .                                  | 21        |
| 2.3.2.1  | Magnus propagator . . . . .                                      | 23        |
| 2.3.2.2  | Crank-Nicolson propagator . . . . .                              | 24        |
| 2.4      | Random Electronic Stopping Power Calculations . . . . .          | 26        |
| 2.4.1    | Simplification of Ehrenfest dynamics . . . . .                   | 27        |
| 2.4.2    | Trajectory sampling and averaging . . . . .                      | 29        |
| <b>3</b> | <b>Electronic Stopping Power without Projectile Basis in LiF</b> | <b>33</b> |
| 3.1      | Stopping Powers of Proton and Antiproton in LiF . . . . .        | 34        |
| 3.2      | Fractional charges analysis . . . . .                            | 39        |
| 3.3      | Isolated ions analysis . . . . .                                 | 40        |
| <b>4</b> | <b>Adapting Equations with Moving Projectile Basis</b>           | <b>45</b> |
| 4.1      | Projectile Position Dependency . . . . .                         | 45        |
| 4.1.1    | Change of reference frames . . . . .                             | 46        |
| 4.1.2    | Properties and roles of $\hat{D}$ . . . . .                      | 51        |
| 4.1.3    | Numerical study of $\hat{D}$ . . . . .                           | 55        |
| 4.2      | Modifications in Propagators . . . . .                           | 58        |
| <b>5</b> | <b>Numerical Development and Validation of Code</b>              | <b>61</b> |
| 5.1      | Implementation and Optimisation . . . . .                        | 61        |
| 5.1.1    | Tracking projectile basis . . . . .                              | 61        |

|          |                                                                     |            |
|----------|---------------------------------------------------------------------|------------|
| 5.1.2    | Predictor-corrector scheme . . . . .                                | 63         |
| 5.1.3    | Partial calculations of matrices . . . . .                          | 64         |
| 5.2      | Functionality Test . . . . .                                        | 66         |
| 5.2.1    | Energy treatments in atomic systems . . . . .                       | 66         |
| 5.2.2    | Replace physical atoms by ghost sites . . . . .                     | 68         |
| 5.2.3    | Compare projectile with and without basis . . . . .                 | 69         |
| 5.2.4    | System's symmetry test . . . . .                                    | 71         |
| <b>6</b> | <b>Electronic Stopping Power with Projectile Basis in Li and Al</b> | <b>73</b>  |
| 6.1      | Convergence Parameters . . . . .                                    | 73         |
| 6.1.1    | Cluster geometry - length . . . . .                                 | 76         |
| 6.1.2    | Cluster geometry - radius . . . . .                                 | 77         |
| 6.1.3    | Basis quality - target . . . . .                                    | 78         |
| 6.1.4    | Basis quality - projectile . . . . .                                | 80         |
| 6.2      | Random Electron Stopping Power in Lithium . . . . .                 | 85         |
| 6.2.1    | Hydrogen in lithium . . . . .                                       | 85         |
| 6.2.2    | Helium in lithium . . . . .                                         | 88         |
| 6.3      | Channeling Stopping Power in Aluminum . . . . .                     | 89         |
| 6.3.1    | Hydrogen channeling . . . . .                                       | 92         |
| 6.3.2    | Helium channeling . . . . .                                         | 94         |
| 6.4      | Random Electronic Stopping Power in Aluminum . . . . .              | 96         |
| 6.4.1    | Hydrogen in aluminum . . . . .                                      | 96         |
| 6.4.2    | Helium in aluminum . . . . .                                        | 98         |
| 6.4.3    | Aluminum in aluminum . . . . .                                      | 101        |
| <b>7</b> | <b>Conclusion</b>                                                   | <b>107</b> |
| 7.1      | Achievements . . . . .                                              | 108        |
| 7.2      | Perspectives . . . . .                                              | 110        |
|          | <b>References</b>                                                   | <b>112</b> |

# List of Figures

|                                                                                                     |    |
|-----------------------------------------------------------------------------------------------------|----|
| 1.1.1 Illustrated setup of the JANNuS facility in CEA Saclay . . . . .                              | 3  |
| 2.2.1 Mixed basis technique applied on a lithium cluster . . . . .                                  | 14 |
| 2.4.1 Energy profile of hydrogen piercing through in lithium . . . . .                              | 29 |
| 2.4.2 Polar symmetry sampling of impact parameters . . . . .                                        | 30 |
| 2.4.3 Angle induced errors and new sampling technique . . . . .                                     | 31 |
| 3.1.1 Views of LiF [111] and the running stopping power . . . . .                                   | 34 |
| 3.1.2 Crystal orientation sensitivity of the RESP in LiF . . . . .                                  | 35 |
| 3.1.3 RESP of proton and antiproton in LiF . . . . .                                                | 36 |
| 3.1.4 Channeling SP of proton and antiproton in LiF . . . . .                                       | 38 |
| 3.2.1 Fractional charges analysis of RESP in LiF . . . . .                                          | 39 |
| 3.3.1 $\Delta E$ of proton and antiproton in isolated $\text{Li}^+$ and $\text{F}^-$ ions . . . . . | 41 |
| 3.3.2 SCS and first excitation energy in systems of isolated $\text{F}^-$ ion . . . . .             | 42 |
| 3.3.3 Electron population change of the $\text{F}^-$ orbitals . . . . .                             | 43 |
| 4.1.1 Energy approximation of $m_q v^2$ with $E_{-iD}$ . . . . .                                    | 57 |
| 4.2.1 Electron conservation errors with propagators . . . . .                                       | 60 |
| 5.1.1 Predictor-corrector scheme . . . . .                                                          | 64 |
| 5.2.1 Energy treatment of helium hitting proton . . . . .                                           | 67 |
| 5.2.2 Projectile He with a target or ghost H . . . . .                                              | 69 |
| 5.2.3 Presence and absence of projectile basis for proton in He . . . . .                           | 70 |
| 5.2.4 Role-switching test between H and He . . . . .                                                | 71 |
| 6.1.1 Löwdin charge stabilization and the averaged SP of hydrogen in aluminum . . . . .             | 74 |
| 6.1.2 Channeling SP in relation to lengths . . . . .                                                | 77 |
| 6.1.3 Channeling SP in relation to radius . . . . .                                                 | 78 |
| 6.1.4 Convergence in relation to target basis quality in aluminum . . . . .                         | 79 |
| 6.1.5 Running SP of hydrogen in aluminum . . . . .                                                  | 81 |
| 6.1.6 Convergence in relation to projectile basis quality in aluminum . . . . .                     | 82 |
| 6.1.7 Convergence in case of identical basis . . . . .                                              | 84 |
| 6.2.1 RESP of hydrogen in lithium at different velocities . . . . .                                 | 86 |
| 6.2.2 RESP of helium in lithium at different velocities . . . . .                                   | 88 |
| 6.3.1 Center shifting of the aluminum cluster . . . . .                                             | 90 |
| 6.3.2 Stopping powers of hydrogen in aluminum with different cluster centers . . . . .              | 91 |
| 6.3.3 Channeling SP of hydrogen in aluminum at different velocities . . . . .                       | 93 |
| 6.3.4 Channeling SP of helium in aluminum at different velocities . . . . .                         | 95 |
| 6.4.1 RESP of hydrogen in aluminum as a function of velocity . . . . .                              | 97 |
| 6.4.2 RESP of helium in aluminum as a function of velocity . . . . .                                | 99 |

|                                                                       |     |
|-----------------------------------------------------------------------|-----|
| 6.4.3 Stopping powers of ions in various solids . . . . .             | 101 |
| 6.4.4 RESP of various ions in aluminum from SRIM . . . . .            | 101 |
| 6.4.5 RESP of aluminum in aluminum at different velocities . . . . .  | 103 |
| 6.4.6 RESP in logscale of different projectiles in aluminum . . . . . | 106 |

# Chapter 1

## Introduction

The subject of this thesis, though very specific, is generally inspired by the ongoing studies of nuclear safety and materials damages in CEA, the French Alternative Energies and Atomic Energy Commission. In the course of this introduction, we will briefly talk about how the role of nuclear energy has evolved and why the ion irradiation experiments are important for the nuclear safety research. We will have a look at the experimental setups of such experiments and discuss about their need of theoretical references. Some other fields of study that involve the ion irradiation will also be mentioned. Then we will focus on the definition of electronic stopping power (SP) which is a way to quantify the electronic excitations caused by the ion irradiation of materials and some early analytical models that attempt to evaluate this property. At the end of this chapter, we will introduce the simulation program in which we implement our first-principles solutions to the electronic SP calculations.

### 1.1 Research Inspirations

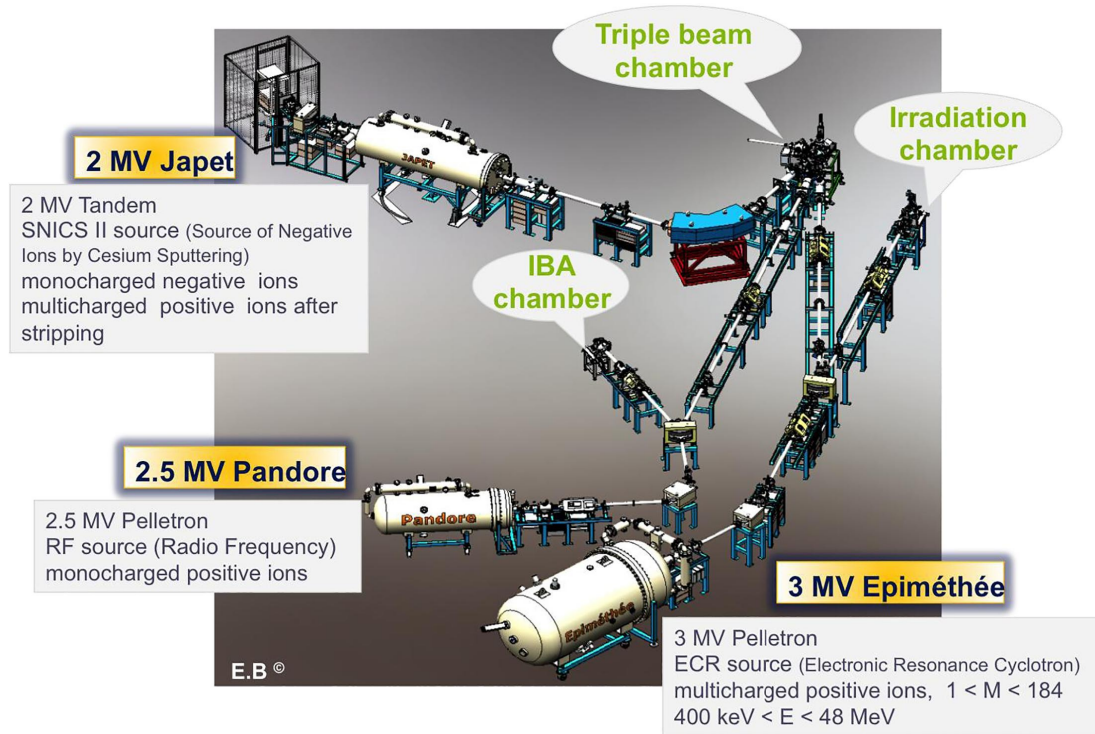
A neutron capture anomaly was discovered by Enrico Fermi in 1934 and was further proved to be the nuclear fission reaction by Lise Meitner, Otto Frisch, Otto Hahn and Fritz Strassmann in 1939 [1]. Ever since, massive attentions have been brought into the research and development of this new energy source. Although most of the early efforts were poured into weapon-related applications due to the second world war [2], in 1953 the US president Dwight Eisenhower declared the shift of focus in nuclear research from military to peaceful civilian use [3].

Nowadays, nuclear power plants generate 16% of the electricity supply worldwide and France alone produces 75% of its electricity with nuclear power [4]. Facing a worsening global climate and an urgent need to curb greenhouse gases emission [5], alternative energy sources are called upon to replace the traditional burning of fossil fuels. Nuclear energy, with its capacity of mass production and delivery, becomes an important asset to meet the tremendous energy demand of our modern technology-oriented society [6].

However, there are several downsides of nuclear energy generation, with safety being a major concern. Nuclear plant accidents like those which happened in Three Mile Island (1979), Chernobyl (1986) and Fukushima (2011) have been fatal for individuals and catastrophic for societies [7]. Nuclear safety is therefore a crucial research topic to limit the exposures to radiation, to reduce the probabilities of accidents and to mitigate the eventual damages from such accidents [8]. The safety of a nuclear plant can be hindered by the degradation of reactor materials which are under constant neutron irradiation. The properties of irradiated materials are permanently changed by either crystal defects or transmutation [9]. While many experiments of nuclear materials damages are carried out using neutrons to mimic the radioactive environment inside nuclear reactors [10, 11, 12], these are delicate to maneuver with the radiation protection equipment and are expensive to install. Swift ion beam, on the other hand, is a popular substitution to the neutron beam at relatively lower costs, and allows more flexible experimental controls during the irradiation [13, 14, 15]. The Joint Accelerators for Nanosciences and Nuclear Simulation (JANNuS) platforms, situated in both the Paris-Saclay University and the CEA site at Saclay, are exemplary in using ion accelerators to emulate neutron-induced damages in nuclear materials [16, 17].

In the following sections we will first introduce the facility in JANNuS as an example of experimental setups for ion beam irradiation. We will then talk about the common practice to benchmark the experimental data against the prediction from SRIM, the Stopping and Range of Ions in Matter [18, 19] code, and the drawbacks of this approach. At last, a few more research areas involving the ion radiations other than the nuclear safety will be presented.

### 1.1.1 Experiments



**Figure 1.1.1:** Illustrated setup of the JANNuS facility in CEA Saclay [17]. The three ion accelerators are named as Japet, Pandore and Epiméthée. The triple beam chamber can host single, duel and triple beam irradiation. The other irradiation chamber linked to the accelerator Epiméthée is in charge of single beam irradiation. The IBA chamber is responsible for Ion Beam Analysis.

Ion accelerators are key ion sources in the experimental setups of ion beam irradiation [14, 15], and the combination of multiple beam lines can produce radiations more similar to that in the nuclear environment than using a single beam line [17]. More specifically, proton and helium beams need to be combined in ion irradiation experiments to mimic the transmutation effects on the micro-structure of reactor materials (cavities, dislocations, secondary phases, etc.) [20]. The JANNuS facility in the CEA site in Saclay, as illustrated in figure 1.1.1, is one of such multi-beam installations with three ion accelerators and three irradiation and analysis chambers. This facility enables the implantation of a large variety of ions of different masses in a vast range of solid materials [17].

One of the interesting properties resulted from the ion implantation is the depth profile or the damage profile which describes the concentration of implanted ion as a function of its implantation depth inside a material. Another important property that can be derived from the depth profile is the stopping power which constitutes the core subject

of this thesis and will be further explained in a later section. Studies of depth profiles and stopping powers are abundant [21, 22, 23] and as a common practice they are often benchmarked against the predictions from one particular empirical program SRIM [18, 19]. Based on the Lindhard linear-response formula, the local-density approximation and many empirical rules, SRIM is capable of giving predictions by fitting mathematical models to the experimental data in its database after some scaling and corrections [19]. While we will briefly talk about the Lindhard model in a later section, we will not provide a detailed explanation of the SRIM algorithms which is outside the scope of this work.

The important message that we get is that since SRIM is heavily dependent on the collection of experimental data, its accuracy is put into doubt in cases where such data are scarce [24] like helium ion in lithium, iron in nickel and nickel in nickel [18]. Many authors have reported misleading stopping power information from SRIM for heavy ions in light target materials [25, 26] and at velocities below the Bragg's peak [24]. To resolve this uncertainty towards the gold standard set by SRIM among the experimentalists, first-principles approaches like ours need to be developed to serve as a second reference to the experimental results.

## 1.1.2 Applications

There are many other fields of applications besides nuclear reactor materials that benefit from the understanding of ion radiations. In medicine, particle radiotherapy using proton or carbon ions is playing an increasingly important role in the treatment of cancer cells thanks to its superior biological effectiveness (more precise and focused cellular damaging) comparing to the traditional X-rays treatment [27, 28, 29]. In materials science, ion beam processing and ion implantation are used to create specific functionalities to electronic devices and enhance materials properties [30, 31, 32]. Heavily present in space, ion irradiation is also frequently studied for the purpose of space radiation protection and the chemical evolution of planetary environment [33, 34, 35].

In this section we have explained under the context of nuclear safety the importance of ion irradiation studies on reactor materials. Theoretical first-principles research is necessary to provide references for experimental measurements of ion-induced properties like the stopping power. The next section will focus on the definition of stopping power and the evolution of early analytical models to calculate the electronic part of this quantity.

## 1.2 Electronic Stopping Power

As mentioned earlier, the stopping power of ions inside the irradiated materials is an important property to be studied during the ion irradiation. The definition of the stopping power and the distinction between the nuclear and electronic stopping power will be given in the first part of this section. The second part of this section will present in a brief manner the early evolution of analytical models that attempt to evaluate the electronic stopping power.

### 1.2.1 Definition

An ion projectile with a finite velocity  $v$  possesses kinetic energy  $E_{kin}^{proj}(v)$ . The loss of its kinetic energy as it advances a depth of  $x$  inside the target materials is measured as the stopping power [36]

$$S(v) = -\frac{dE_{kin}^{proj}(v)}{dx}. \quad (1.2.1)$$

The negative sign in equation (1.2.1) indicates thus the energy loss. The relation between the stopping power and the general depth  $L$  of ion implantation is obtained based on the Continuous Slowing Down Approximation (CSDA) [36]

$$L = \int_0^{E_0} \frac{dE_{kin}^{proj}(v)}{S(v)}, \quad (1.2.2)$$

where  $E_0$  stands for the initial value of projectile kinetic energy.

Several energy exchange processes can happen when the projectile ion encounters the target atoms, notably the transfer of center-of-mass momentum and the electronic excitation or ionization [36]. The first process involves classical mechanics and is responsible for the nuclear stopping power  $S_n$ , while the second process involving quantum mechanics attributes to the electronic stopping power  $S_e$ . The total stopping power  $S(v)$  can therefore be split into two parts [37]

$$S(v) = S_n(v) + S_e(v). \quad (1.2.3)$$

The work of this thesis, under the scope of quantum mechanics, focuses solely on the electronic contribution  $S_e$  to the stopping power. In the next part we will present a few early analytical models as scientists aim to calculate the electronic stopping power.

## 1.2.2 Early analytical models

Even though a quantum mechanical problem, the calculation of electronic stopping power has already been attempted with classical approaches [38]. Back in 1911 Rutherford [39] measured the deflection of  $\alpha$  and  $\beta$  particles in a thin layer of gold foil. This can be readily considered as an experimental setup for the stopping power. Soon later in 1930 Bethe [40] came up with a classical model where the interactions between a projectile and the target electrons are treated as binary Coulomb collisions. The celebrated Bethe formula writes

$$S_e(v) = \frac{4\pi n}{m_e v^2} Z^2 k_e^2 e^4 \log\left(\frac{2m_e v^2}{I}\right). \quad (1.2.4)$$

Though having a limited lower bound of valid projectile velocity, this formula describes the general characters of the electronic stopping power  $S_e(v)$ : 1) a direct relation to the electron density  $n$  and the projectile charge  $Z$ ; 2) a quadratic decrease with  $v^2$  at large velocities.  $k_e$  is the Coulomb's constant and  $I$  contains the screening and quantum mechanical effects. A complementary formula for the low velocity region was derived by Fermi and Teller in 1947 [41].

$$S_e(v) = Z^2 \frac{2v}{3\pi} m_e \frac{k_e^2 e^4}{\hbar^3} \log(\pi \hbar v_F k_e e^2). \quad (1.2.5)$$

This equation describes a linear relation with  $v$  below the Fermi velocity  $v_F$  and is the first to consider the degenerate electron gas.

In real materials the interpretation of these two formulas is often empirical due to the ambiguous definition of  $n$  and  $Z$ . As theories advance towards first-principles methods, Lindhard hit a major milestone in 1963 [42, 43] with his general linear response model

$$S_e(v) = 2Z^2 \frac{e^2}{\pi v^2} \int_0^\infty \frac{dk}{k} \int_0^{kv} \omega d\omega \Im\left(\frac{-1}{\varepsilon(k, \omega)}\right). \quad (1.2.6)$$

The key element in this formula is the linear dielectric response  $\varepsilon$  inside the energy-loss function  $\Im(-\varepsilon(k, \omega)^{-1})$ . Described by frequency  $\omega$  and wavenumber  $k$ ,  $\varepsilon(k, \omega)$  contains all the information about the system such as excitation energies and many-body effects. Originally Lindhard's dielectric response  $\varepsilon(k, \omega)$  is intended for *jellium* models only, but the recent work of Shukri *et al.* [44] has improved this function to work with non-homogeneous systems. However powerful the linear response approach is, it still fails to capture the non-linear properties associated to negatively charged particles like the Barkas [45] and

negative Barkas [46] effects since all information about the charge sign is erased by the quadratic term  $Z^2$ . Breakthroughs in non-linear *ab initio* methods were stalled until the arrival of Density Functional Theory (DFT) and its time-dependent derivations that we will discuss in more details in Chapter 2.

## 1.3 Simulation Program MOLGW

First developed by Bruneval *et al.* [47], the code MOLGW uses Gaussian-Type Orbitals (GTO) basis to compute excited electronic states in finite systems. DFT is fully included in MOLGW with a Self-Consistent Field (SCF) scheme to prepare the ground state, and Real-Time (RT) Time-Dependent DFT (TDDFT) is implemented among many post-treatment options. The current version of the code assigns basis functions only to target atoms whose positions are fixed. Although providing good results for projectiles with no electrons like proton, antiproton and  $\alpha$ -particles [48, 49, 46], the lack of basis on the projectile is inadequate to simulate interesting experimental cases where the projectile possesses a finite number of electrons. In order to capture the dynamics of electrons that belong to the projectile, we need to enable the code with moving basis functions localized on the projectile. Not only is this a physical problem to solve, but also a technical problem as the time and space complexities of the calculations increase.

In the following discussions we will first recall the fundamental theories behind this work in Chapter 2, especially for situations without projectile basis functions. Chapter 3 goes on to present a side study of proton and antiproton stopping powers in LiF without projectile basis. Then we will walk through the theoretical development involving the moving projectile basis in Chapter 4. In Chapter 5 we will begin by explaining the numerical techniques adopted to implement the time propagation and to optimize the run-time and the memory occupation. We will next demonstrate in the same chapter the validation of our code by several functionality tests using simple atomic systems. Finally in Chapter 6 we will discuss about the simulation parameters for the convergence of stopping powers of light and heavier projectiles inside solid clusters before exhibiting some final results.



# Chapter 2

## Fundamental Theories and Technical Background

In this chapter we will briefly review some key concepts supporting the numerical simulations of the stopping power from first-principles. We will begin with a short summary of the Density Functional Theory (DFT) and its time-dependent variation TDDFT. Then we will discuss about the choice of basis set in MOLGW, as well as the approximations adopted to minimize the costs of the 4-center integral calculations. Matrix expressions in orthogonal basis without projectile basis functions will be briefly recapitulated, and the two main propagators used in MOLGW for the real-time propagation will be compared. At last we will present the techniques used for obtaining the random electronic stopping power (RESP) from single-trajectory stopping powers. Atomic units ( $e^2 = \hbar = m = 1$ ) are used from now on if no other units are specified.

### 2.1 From Stationary to Time-Dependent DFT

The physical mechanism of electronic stopping power is an ion-electron problem best described by the full many-body Schrödinger equation [38]

$$\hat{H}\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) = E\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N), \quad (2.1.1)$$

where  $\hat{H}$  denotes the full Hamiltonian for a system of  $N$  electrons and  $E$  is the total energy of the system. The detailed description of  $\hat{H}$  is as follows [50]

$$\hat{H} = -\frac{1}{2} \sum_{i=1}^N \nabla_{\mathbf{r}_i}^2 + \sum_{i=1}^N \sum_{j>i}^N w(|\mathbf{r}_i - \mathbf{r}_j|) - \sum_{i=1}^N v(\mathbf{r}_i) = \hat{T} + \hat{W} + \hat{V}. \quad (2.1.2)$$

In the first part of equation (2.1.2),  $\mathbf{r}_i$  denotes the electron position.  $w(|\mathbf{r}_i - \mathbf{r}_j|)$  is the potential for interactions between electrons and  $v(\mathbf{r}_i)$  the external potential acting upon the electrons. In the second part we rewrite the three terms from the first part into three operators.  $\hat{T}$  is the kinetic operator,  $\hat{W}$  the electron-electron interaction operator and  $\hat{V}$  the external potential operator.

If there are only a few electrons, we can solve equation (2.1.1) analytically with the wave functions  $\Psi$  being a function of  $3N$  variables representing the three-dimensional positions of the electrons. However, this analytical work is impossible for a larger systems and some approximations are required. The DFT is one of the most popular approximation methods thanks to the following two statements [51]. In 1964 Hohenberg and Kohn [52] proposed that all physical properties of a ground-state system can be extracted from its ground-state electron density  $\rho(\mathbf{r})$  since this quantity is in unique correspondence to the external potential  $v(\mathbf{r})$  thus to the entire Hamiltonian. This means that instead of solving the complex  $3N$ -variable  $\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)$  we can calculate  $\rho(\mathbf{r})$  that contains only 3 variables. Soon later in 1965 Kohn and Sham [53] introduced the non-interacting kinetic energy operator which broke the many-body equation (2.1.1) into a collection of single-body equations. The ground-state many-body wave function  $\Psi$  can therefore be transformed into a single Slater determinant  $\Psi_S$

$$\Psi_S(\mathbf{r}_1, \dots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\mathbf{r}_1) & \psi_2(\mathbf{r}_1) & \dots & \psi_N(\mathbf{r}_1) \\ \psi_1(\mathbf{r}_2) & \psi_2(\mathbf{r}_2) & \dots & \psi_N(\mathbf{r}_2) \\ \vdots & \vdots & & \vdots \\ \psi_1(\mathbf{r}_N) & \psi_2(\mathbf{r}_N) & \dots & \psi_N(\mathbf{r}_N) \end{vmatrix}, \quad (2.1.3)$$

where the single-particle functions  $\psi_i(\mathbf{r})$  are orthonormal and satisfy the Kohn-Sham (KS) equation with the KS Hamiltonian  $H_{KS}(\mathbf{r})$

$$\left( -\frac{1}{2} \nabla_{\mathbf{r}}^2 + v_{KS}[\rho](\mathbf{r}) \right) \psi_i(\mathbf{r}) = H_{KS}(\mathbf{r}) \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}). \quad (2.1.4)$$

The KS potential in the above equation is defined as

$$v_{KS}[\rho](\mathbf{r}) = v(\mathbf{r}) + v_H[\rho](\mathbf{r}) + v_{xc}[\rho](\mathbf{r}), \quad (2.1.5)$$

where  $v(\mathbf{r})$  denotes the external potential,  $v_H[\rho](\mathbf{r})$  the Hartree potential and  $v_{xc}[\rho](\mathbf{r})$  the exchange-correlation (xc) potential.

However, there is a catch to such simplifications. The details of many-body interactions are now hidden in the exchange-correlation potential  $v_{xc}$  that has no exact expression [51]. We have no choice but to use approximate functionals to estimate this term. Originally Kohn and Sham [53] has proposed the Local-Density Approximation (LDA) functional alongside their single-particle solutions. This functional integrates the xc energy of a homogeneous reference system evaluated at its local density to give the global xc energy of an inhomogeneous system. Although not the most accurate, LDA became a popular method as it possesses many correct features like the sum rules and the scaling properties [54]. Later improvements on LDA include the Generalized Gradient Approximation (GGA), meta-GGA and hybrid functionals. It has been pointed out by many authors [49, 46, 55, 56] that the calculations of electronic stopping power are weakly influenced by the choice of  $v_{xc}$  functionals. Therefore in the scope of our study the less expensive LDA is considered as the best compromise between costs and accuracy.

The DFT plays an essential role as the starting point of our study and gives us the ground state information of the target-projectile system. At the same time, the dynamical nature of the electronic stopping power means that we have to simulate time-dependent properties like the total energy  $E(t)$ . This is where we use the time-dependent Schrödinger equation (TDSE)

$$i\frac{\partial}{\partial t}\Psi(t) = \hat{H}(t)\Psi(t). \quad (2.1.6)$$

In order to construct the TDDFT, we need to show that the time-dependent density  $\rho(\mathbf{r}, t)$  has a unique one-to-one correspondence to the time-dependent potential  $v(\mathbf{r}, t)$ . The proof of this was provided by Runge and Gross [57] in 1984. Furthermore, we would like to have a practical formalism similar to that of Kohn and Sham to reduce the many-body problem into a single-particle one. Thankfully in 1999 van Leeuwen [58] came up with the confirmation that the electron density  $\rho(\mathbf{r}, t)$  of an interacting system can indeed be obtained from a non-interacting system. Combining these two new theorems we write the

single-electron Time-Dependent Kohn-Sham (TDKS) equation

$$i\frac{\partial}{\partial t}\psi_i(\mathbf{r}, t) = \hat{H}_{KS}(\mathbf{r}, t)\psi_i(\mathbf{r}, t) = \left( -\frac{1}{2}\nabla_{\mathbf{r}}^2 + v_{KS}[\rho](\mathbf{r}, t) \right)\psi_i(\mathbf{r}, t). \quad (2.1.7)$$

This constitutes the backbone of our RT-TDDFT development where the real time evolution of the system is discretized into tiny time steps for numerical simulations. From here on we will drop the notation  $KS$  for the Kohn-Sham Hamiltonian unless mentioned otherwise.

## 2.2 Choice of Basis Sets

We have discussed in the previous section that in both DFT and TDDFT the many-body wave functions  $\Psi$  can be reduced to Slater determinants constructed by a series of orthonormal one-particle functions  $\psi_i$ . These single-body functions can then be represented by linear combinations of basis functions  $\phi_{\alpha}$  with coefficients  $C_{\alpha i}$  that are not necessarily orthogonal [50]

$$\psi_i(\mathbf{r}, t) = \sum_{\alpha} C_{\alpha i}(t)\phi_{\alpha}(\mathbf{r}). \quad (2.2.1)$$

Together these basis functions form a basis set, and the quality or the completeness of the basis set is determined by the parametrization of  $\phi_{\alpha}$ . Ideally, the more complete the basis set the more accurate it describes the systems since it will have a better coverage of the Hilbert space [59, 50]. Even though in reality the true basis completeness is only an ideological concept, researchers have succeeded in developing very complex basis sets to approach this goal. Many of those basis sets are available at the Basis Set Exchange (BSE) library, first constructed by Schuchardt *et al.* [60] and later updated by Pritchard and co-authors [61].

There exist several types of basis functions. Let us first comment on the plane-wave basis functions which are independent of the ion positions  $\mathbf{R}_A(t)$

$$\psi_i(\mathbf{r}, t) = \sum_{\mathbf{g}} C_{\mathbf{g}}(t)e^{i\mathbf{g}\cdot\mathbf{r}}. \quad (2.2.2)$$

Basis functions of this form allow direct calculations of forces exercised on the projectile ion without treating the movement of basis centers that follow the advancement of the projectile center [38]. Another advantage of plane-wave functions is their natural compatibility with

periodic systems [38]. However, the downside of this choice is the huge computational cost of the bulk model and the inability to simulate deep core electrons [38]. Calculation programs such as Qbox/Qb@ll [62, 63] and GPAW [64, 65] are examples of plane-wave basis approach.

In our program MOLGW [47] a second type of basis sets is applied. These basis functions  $\phi_\alpha(\mathbf{r} - \mathbf{R}_{A_\alpha}(t))$  are real and Gaussian-like and are localized on the ion centers. They are dependent on the ion positions and require special treatments when the ions move. One advantage of these Gaussian-Type Orbital (GTO) functions over the plane-wave basis is to give a more natural representation of bounded electrons around the ion. At the same time they can describe the excitation process through the use of polarization and diffuse functions [38]. Moreover, calculations using localized basis sets can easily be done on computers with small to medium memory size since all operators in equation (2.1.2) can be stored as matrix coefficients [66].

In the previous version of the MOLGW code all basis functions are static and none are localized on the projectile. The new development presented in this thesis aims to enable some basis functions to move along with the projectile. The differentiation between the two scenarios, with and without moving projectile basis, will be discussed at length in Chapter 3. Some other programs using the localized moving basis sets include SIESTA [66] and CP2K [67].

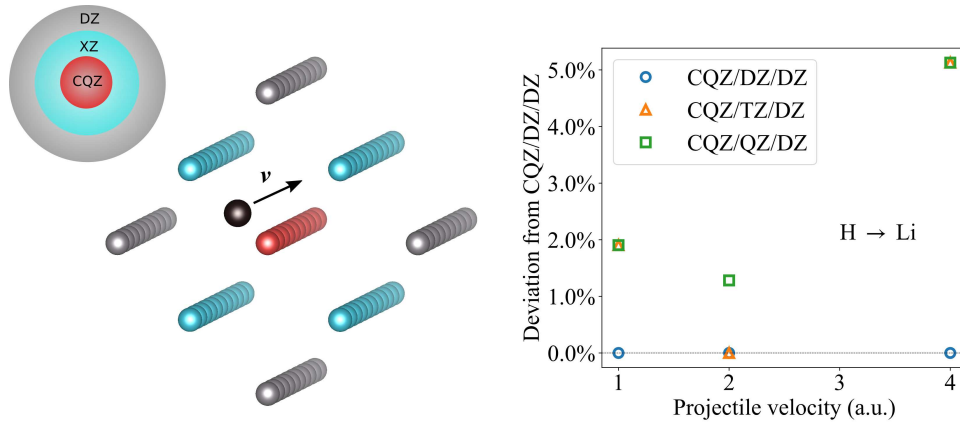
In the following parts of this section, we will first introduce a modeling technique where mixed basis qualities are applied on target atoms to reduce computational costs. Afterwards, we will demonstrate the matrix representation of some key DFT quantities before explaining the approximations used to calculate the 4-center integrals resulted from the Hartree potential  $v_H$  in equation (2.1.5).

## 2.2.1 Mixed Dunning basis technique

Dunning and his coworkers [68, 69, 70] have defined the correlation-consistent polarized Valence  $X$ -Zeta (cc-pVXZ) basis sets, where  $X = D, T, Q, 5, 6, \dots$  is the cardinal number that describes the basis quality. The higher the value of  $X$ , the more complete is the basis. From this point on, we will abbreviate the cc-pVXZ basis as  $XZ$ . Other variance of the Dunning series includes the augmented or diffuse aug-cc-pVXZ (abbreviated as AXZ) basis set, the core-valence cc-pCVXZ (CXZ) basis set and the augmented core-valence

aug-cc-pCVXZ (ACXZ) basis set, all available in the Basis Set Exchange (BSE) library.

Using high-quality basis set all over the system is sometimes redundant and very expensive for the computers. One way to economize on the basis set is to apply them with mixed qualities in the system [48]. This means that the most expensive basis are only used on target atoms with significant contribution to the stopping power which are usually the closest to the projectile trajectory. Layers of atoms farther to the trajectory are then described by less complete basis. Figure 2.2.1 illustrates how this technique is employed on a lithium cluster with three different basis qualities from CQZ on the column of atoms nearest to the projectile trajectory to the standard XZ on farther atoms then the least costly DZ on the out-most layer. We also show in this figure how the RESP is insensitive to the second layer basis quality. At  $v = 1.0$  (25 keV) and 4.0 a.u. (400 keV) of the hydrogen projectile, the RESP value is converged from  $X = T$  on. At  $v = 2.0$  a.u. (100 keV) the RESP is the same for  $X = D$  and T, with a small deviation of less than 2% at  $X = Q$ . This insensitivity of RESP towards the basis quality on less impacted target atoms makes the mixed basis technique a practical tool to reduce the computational expenses.



**Figure 2.2.1:** Mixed basis technique applied on a lithium cluster (94 atoms) and the convergence of RESP of hydrogen at different  $v$ . On the left side we demonstrate the technique. The proton projectile (TZ) and its trajectory are illustrated by a black sphere and a black arrow. Three qualities of basis are used on the lithium target. Red spheres indicate atoms with CQZ basis, blue spheres are for atoms with XZ basis ( $X = D, T, Q$ ), and grey spheres represent atoms with DZ basis. The plan-view of the clusters is provided on the upper right of the image where each circle represents a layer of atoms selected for a specific basis quality. On the right side we compare the RESP of hydrogen in lithium obtained at three velocities  $v = 1.0, 2.0$  and 4.0 a.u., with results from the CQZ/DZ/DZ mixture as the reference for deviation.

## 2.2.2 Matrix representations in localized basis sets

A major advantage of using localized basis sets is to facilitate calculations of physical problems by transforming equations into matrix expressions [66]. We will now define a few quantities in the GTO basis sets for the stationary systems. The most important quantity in DFT is the one-particle electron density

$$\rho(\mathbf{r}) = \sum_{i=1}^N |\psi_i(\mathbf{r})|^2, \quad (2.2.3)$$

which is normalized to the total electron number

$$\int \rho(\mathbf{r}) d\mathbf{r} = N. \quad (2.2.4)$$

Depending on the basis set used, a system can have as many energy states as the number of basis functions  $N_{BF}$ . In practice, only the occupied states are needed to calculate the electron density thus we can reformulate equation (2.2.3) into

$$\rho(\mathbf{r}) = \sum_{i=1}^{occ} f_i \psi_i(\mathbf{r}) \psi_i^*(\mathbf{r}), \quad (2.2.5)$$

with  $f_i$  being the occupation number of state  $i$ . Let us now look at the density in its matrix form. Recall equation (2.2.1) where we expand the one-body wave functions  $\psi_i$  in a basis set. Inserting it into the above density expression gives us [50]

$$\begin{aligned} \rho(\mathbf{r}) &= \sum_{i=1}^{occ} f_i \sum_{\alpha} C_{\alpha i} \phi_{\alpha}(\mathbf{r}) \sum_{\beta} C_{\beta i}^* \phi_{\beta}^*(\mathbf{r}) \\ &= \sum_{\alpha\beta} \left[ \sum_{i=1}^{occ} f_i C_{\alpha i} C_{\beta i}^* \right] \phi_{\alpha}(\mathbf{r}) \phi_{\beta}(\mathbf{r}) \\ &= \sum_{\alpha\beta} P_{\alpha\beta} \phi_{\alpha}(\mathbf{r}) \phi_{\beta}(\mathbf{r}). \end{aligned} \quad (2.2.6)$$

Here we represent the general case where the coefficients  $C_{\alpha i}$  can be either real or complex and the basis functions  $\phi_{\alpha}(\mathbf{r})$  are always real. The density matrix  $P_{\alpha\beta}$  in the matrix form is thus

$$P = C F C^H, \quad (2.2.7)$$

with  $F$  being the occupation matrix that is diagonal and has real eigenvalues  $f_i$  and  $C$  the coefficient matrix whose columns correspond to the states  $i$ . As the occupation number  $f_i$  for unoccupied states is simply 0, we can reduce the dimension of  $F$  to match with the number of occupied states  $N_{OCC}$  and furthermore reduce the dimension of  $C$  to  $N_{BF} \times N_{OCC}$ .  $P$  is easily proven to be Hermitian

$$P^H = (CFC^H)^H = (C^H)^H (CF)^H = CFC^H = P. \quad (2.2.8)$$

Another important quantity defined in the localized basis set is the overlap matrix

$$S_{\alpha\beta} = \langle \phi_\alpha | \phi_\beta \rangle = \int d\mathbf{r} \phi_\alpha(\mathbf{r}) \phi_\beta(\mathbf{r}), \quad (2.2.9)$$

which is a symmetric matrix with real values. If the basis set is orthonormal, the overlap matrix simply becomes the identity matrix. Similarly we can write the Hamiltonian matrix in the localized basis set

$$H_{\alpha\beta} = \int d\mathbf{r} \phi_\alpha(\mathbf{r}) H(\mathbf{r}) \phi_\beta(\mathbf{r}). \quad (2.2.10)$$

Projecting the stationary KS equation (2.1.4) onto the basis functions  $\phi_\beta$  leads to

$$\sum_{\beta} H_{\beta\alpha} C_{\alpha i} = \varepsilon_i \sum_{\beta} S_{\beta\alpha} C_{\alpha i}, \quad (2.2.11)$$

whose matrix form gives us the Roothaan-Hall equation

$$HC = SCE. \quad (2.2.12)$$

The KS Hamiltonian matrix  $H$  can be further broken into

$$H = T + V + V_H + V_{xc}, \quad (2.2.13)$$

where  $T$  is the kinetic energy matrix,  $V$  the external potential matrix,  $V_H$  the Hartree potential matrix and  $V_{xc}$  the exchange-correlation potential matrix.

In equation (2.2.12)  $E$  is a diagonal matrix containing the state energies  $\varepsilon_i$ . Wave functions  $\psi_i$  obtained as solutions of (2.2.12) are always orthonormal, meaning

$$\langle \psi_i | \psi_j \rangle = \delta_{ij}. \quad (2.2.14)$$

Again when expanded in a localized basis set this becomes

$$\sum_{\alpha\beta} \langle \phi_\beta | C_{\beta i}^* C_{\alpha j} | \psi_\alpha \rangle = \sum_{\alpha\beta} S_{\beta\alpha} C_{\beta i}^* C_{\alpha j} = \delta_{ij}. \quad (2.2.15)$$

Writing in matrix form we have a permutable series of orthonormalization conditions that should be satisfied anytime throughout the numerical simulations

$$C^H S C = S C C^H = C C^H S = I. \quad (2.2.16)$$

### 2.2.3 4-center integrals approximations

The product of basis functions  $\phi_\alpha(\mathbf{r})$  associated with the Hartree potential  $v_H[\rho](\mathbf{r})$  in equation (2.1.5) involve 4-center integrals that are heavy to compute due to the number of 4-center combinations. For easier reading inside the brackets we will replace  $\phi_\alpha$  by its index  $\alpha$  in this section. Using the chemists' notation from reference [50] we can express the Hartree integral as [47]

$$(\alpha | v_H | \beta) = \sum_{\gamma\delta} P_{\gamma\delta} (\alpha\beta | \gamma\delta), \quad (2.2.17)$$

where  $P_{\gamma\delta}$  is the density matrix defined in equation (2.2.6). The four-center integral is therefore

$$(\alpha\beta | \gamma\delta) = \int \int d\mathbf{r} d\mathbf{r}' \phi_\alpha(\mathbf{r}) \phi_\beta(\mathbf{r}) \frac{1}{|\mathbf{r} - \mathbf{r}'|} \phi_\gamma(\mathbf{r}') \phi_\delta(\mathbf{r}'), \quad (2.2.18)$$

One way to reduce the calculation costs is to approximate the 4-center integral by the following expression [71]

$$(\alpha\beta | \gamma\delta) \approx \sum_{KQ} (\alpha\beta | K) (K | Q)^{-1} (Q | \gamma\delta). \quad (2.2.19)$$

Under the chemists' notation the 3-center integrals read

$$(\alpha\beta | K) = \int d\mathbf{r} d\mathbf{r}' \phi_\alpha(\mathbf{r}) \phi_\beta(\mathbf{r}) \frac{1}{|\mathbf{r} - \mathbf{r}'|} \phi_K(\mathbf{r}'), \quad (2.2.20)$$

and the 2-center integrals are written as

$$(K|Q) = \int d\mathbf{r} d\mathbf{r}' \phi_K(\mathbf{r}) \frac{1}{|\mathbf{r} - \mathbf{r}'|} \phi_Q(\mathbf{r}'). \quad (2.2.21)$$

The helper functions noted with capital letters  $K$  and  $Q$  constitute the auxiliary basis set which in analogue to the basis functions are real-valued and centered on the atoms. This method is known as Resolution-of-the-Identity (RI) and the quality of this approximation depends on the quality of the auxiliary basis set. Numerically we can evaluate (2.2.19) in different ways. One approach is to split the positive definite 2-center term into square roots and rewrite (2.2.19) as

$$(\alpha\beta|\gamma\delta) \approx \sum_K M_{\alpha\beta}^K M_{\gamma\delta}^K, \quad (2.2.22)$$

where

$$M_{\alpha\beta}^K = \sum_Q (\alpha\beta|Q)(Q|K)^{-1/2}. \quad (2.2.23)$$

We note that the computational time of matrix  $M_{\alpha\beta}^K$  is proportional to  $(N_{BF}N_{ABF})^2$  and can be gigantic as we get to thousands of basis functions (BF) and auxiliary basis functions (ABF) in a hundred-atoms solid system. If all basis functions remain the same during the simulations, we can calculate  $M_{\alpha\beta}^K$  once at the beginning and then cache it for later use. In case of basis functions that move with the ion centers,  $M_{\alpha\beta}^K$  needs to be updated frequently and will result in expensive computation. Moreover it is difficult to track the correspondence between the matrix elements and the basis functions when acquiring the square root  $(Q|K)^{-1/2}$ , thus we cannot resolve to basis selection to optimize the recalculations like we do for other matrices in Chapter 3.

A lighter alternative is to evaluate the inversion of the 2-center integral as it is and reformulate the Hartree term in equation (2.2.17)

$$\begin{aligned} (\alpha|v_H|\beta) &\approx \sum_{\gamma\delta} P_{\gamma\delta} \sum_{KQ} (\alpha\beta|K)(K|Q)^{-1}(\gamma\delta|Q) \\ &\approx \sum_K (\alpha\beta|K)\rho_K. \end{aligned} \quad (2.2.24)$$

Here we have defined a density  $\rho_K$  associated to the auxiliary basis function  $\phi_K(\mathbf{r}')$

$$\rho_K = \sum_Q (K|Q)^{-1} \sum_{\gamma\delta} P_{\gamma\delta}(\gamma\delta|Q), \quad (2.2.25)$$

and we can consider the relation with the electron density

$$\rho(\mathbf{r}') = \sum_K \rho_K \phi_K(\mathbf{r}'). \quad (2.2.26)$$

This comes from the definition of the Hartree potential

$$v_H[\rho](\mathbf{r}) = \int d\mathbf{r}' \frac{1}{|\mathbf{r} - \mathbf{r}'|} \rho(\mathbf{r}'), \quad (2.2.27)$$

which when inserted into equation (2.2.17) gives

$$(\alpha|v_H|\beta) = \int \int d\mathbf{r} d\mathbf{r}' \phi_\alpha(\mathbf{r}) \phi_\beta(\mathbf{r}) \frac{1}{|\mathbf{r} - \mathbf{r}'|} \rho(\mathbf{r}'). \quad (2.2.28)$$

Now if we replace  $\rho(\mathbf{r}')$  by the relation (2.2.26), we can get back to equation (2.2.24). Inside  $\rho_K$  from expression (2.2.25), the inversion of the 2-center integral will take  $O(N_{ABF}^3)$  time to compute while the product of the density matrix and the 3-center integral takes  $O(N_{BF}^2 N_{ABF})$  time. The multiplication of these two parts takes  $O(N_{ABF}^2)$  time. All of these are significantly faster than the calculation of  $M_{\alpha\beta}^K$  which takes  $O(N_{BF}^2 N_{ABF}^2)$  and advantageous when we need to update the 4-center integrals on the flight during the real-time propagation.

## 2.3 Systems Without Projectile Basis

Here we will briefly recall how the matrix expressions can be simplified in an orthogonal basis when no projectile basis is involved. At the same time we will review in a synthesized manner the real-time propagation of wave functions and compare the second-order Magnus (MAG2) propagator with the Crank-Nicolson (CN) propagator in situations without projectile basis.

### 2.3.1 Canonical orthogonalization

In cases where we do not use projectile basis, we can work in an orthogonal basis [72]. A great advantage of this technique, called canonical orthogonalization [73], is to stabilize the Roothaan-Hall solutions by avoiding the use of the often ill-conditioned  $S$  matrix [74]. Let us rewrite equation (2.2.12)

$$S^{-1}HC = CE. \quad (2.3.1)$$

The transformation of matrix  $C$  between a non-orthogonal and an orthogonal basis can be assured by a transformation matrix  $X$  [75]

$$C = XC'. \quad (2.3.2)$$

Considering the orthonormalization condition of  $C$  in equation (2.2.16) we have

$$C^H SC = C'^H X^H S X C' = I. \quad (2.3.3)$$

In order to meet the above condition, matrix  $X$  needs to satisfy

$$X^H S X = I. \quad (2.3.4)$$

Under the canonical orthogonalization, matrix  $X$  can be defined as

$$X = U s^{-1/2}, \quad (2.3.5)$$

where  $U$  is a unitary matrix and  $s$  is the diagonal matrix containing the eigenvalues of overlap matrix  $S$

$$S = U s U^H. \quad (2.3.6)$$

With such a definition,  $X$  indeed satisfies the relation (2.3.4) and possesses a special property

$$X X^H = S^{-1}. \quad (2.3.7)$$

Inserting expressions (2.3.2) and (2.3.7) into equation (2.3.1) we can further transform matrix  $H$  into a Hermitian matrix

$$H' = X^H H X. \quad (2.3.8)$$

This finally leads to the standard eigenvalue problem in the orthogonal basis

$$H' C' = C' E. \quad (2.3.9)$$

To solve the time-dependent DFT problem of impinging projectile we refer to the TDKS equation (2.1.7). For a one-particle wave function expanded in a localized basis this becomes

$$i \frac{\partial}{\partial t} \left( \sum_{\alpha} C_{\alpha i}(t) \phi_{\alpha}(\mathbf{r}) \right) = \hat{H}(t) \sum_{\alpha} C_{\alpha i}(t) \phi_{\alpha}(\mathbf{r}). \quad (2.3.10)$$

In cases where no basis functions are used on the projectile, all  $\phi_{\alpha}(\mathbf{r})$  are invariant in time and are not affected by the time derivative. This allows us to develop the above equation as

$$i \sum_{\alpha} \frac{\partial}{\partial t} C_{\alpha i}(t) \phi_{\alpha}(\mathbf{r}) = \hat{H}(t) \sum_{\alpha} C_{\alpha i}(t) \phi_{\alpha}(\mathbf{r}). \quad (2.3.11)$$

Projecting onto basis functions  $\phi_{\beta}$  gives us

$$i \frac{\partial}{\partial t} C(t) = H(t) C(t). \quad (2.3.12)$$

Similarly, if the wave functions were expanded in an orthogonal basis we would obtain

$$i \frac{\partial}{\partial t} C'(t) = H'(t) C'(t). \quad (2.3.13)$$

## 2.3.2 Real-time propagation

The formal solution of equation (2.1.6) from instant  $t_0$  to  $t$  can be written as [76]:

$$\Psi(t) = \hat{U}(t, t_0) \Psi_0 = \mathcal{T} \exp \left\{ -i \int_{t_0}^t d\tau \hat{H}(\tau) \right\} \Psi(t_0), \quad (2.3.14)$$

where the time-ordered exponential  $\mathcal{T} \exp$  holds the exact expression for the propagator:

$$\hat{U}(t, t_0) = \sum_{n=0}^{\infty} \frac{(-i)^n}{n!} \int_{t_0}^t d\tau_1 \int_{t_0}^t d\tau_2 \cdots \int_{t_0}^t d\tau_n \times \mathcal{T}\{\hat{H}(\tau_1)\hat{H}(\tau_2)\cdots\hat{H}(\tau_n)\}. \quad (2.3.15)$$

In the case of a time independent Hamiltonian, we can omit the time function  $\mathcal{T}$  in (2.3.15) and simplify the solution to be:

$$\Psi(t) = \exp\{-i(t - t_0)\hat{H}\}\Psi(t_0). \quad (2.3.16)$$

Although this expression is not valid for the TDDFT, we can discretize the time range  $[t_0, t]$  into steps  $\Delta t$  so tiny that the Hamiltonian is almost constant between  $t$  and  $t + \Delta t$ . Now we have found a way to use the time independent propagator under the TDDFT, there are many approximations we can adopt to evaluate the exponential term in equation (2.3.16). No matter what techniques we choose, a reliable propagator should fulfill the following three properties of the exact propagator in expression (2.3.15).

**Decomposable.** It can be easily proven from equation (2.3.14) that:

$$\hat{U}(t_1, t_3) = \hat{U}(t_1, t_2)\hat{U}(t_2, t_3). \quad (2.3.17)$$

Under this property, the time discretization breaks the propagator into

$$\hat{U}(t, t_0) = \prod_{i=0}^{N-1} \hat{U}(t_i + \Delta t, t_i). \quad (2.3.18)$$

**Unitary.** This property conserves the orthonormality of wave functions

$$\langle\psi_i(t_1)|\psi_j(t_1)\rangle = \langle\psi_i(t_2)|\psi_j(t_2)\rangle = \delta_{ij}. \quad (2.3.19)$$

Here we define

$$|\psi_i(t_2)\rangle = \hat{U}(t_2, t_1)|\psi_i(t_1)\rangle, \quad (2.3.20)$$

Plugging this as well as its transpose conjugate form into (2.3.19) leads to

$$\langle\psi_i(t_1)|\psi_j(t_1)\rangle = \langle\psi_i(t_1)|\hat{U}^H(t_2, t_1)\hat{U}(t_2, t_1)|\psi_j(t_1)\rangle, \quad (2.3.21)$$

which is only true if  $\hat{U}$  is unitary

$$\hat{U}^H(t_2, t_1)\hat{U}(t_2, t_1) = \hat{I}. \quad (2.3.22)$$

**Time-reversible.** If we propagate a wave function forward from  $t_1$  to  $t_2$

$$\Psi(t_2) = \hat{U}(t_2, t_1)\Psi(t_1), \quad (2.3.23)$$

then propagate it backwards from  $t_2$  to  $t_1$

$$\Psi(t_1) = \hat{U}(t_1, t_2)\Psi(t_2), \quad (2.3.24)$$

we expect to obtain the same state  $\Psi(t_1)$ . Considering that  $\hat{U}$  is unitary, this can be translated into

$$\hat{U}(t_1, t_2) = \hat{U}(t_2, t_1)^H = \hat{U}(t_2, t_1)^{-1}. \quad (2.3.25)$$

The two main propagator in MOLGW are the second-order Magnus (MAG2) propagator and the Crank-Nicolson (CN) propagator. Both propagators are numerically tested to be quasi-decomposable when used with time steps less than a few attoseconds. In the following sections we will see how both propagators are time-reversible and unitary without projectile basis.

### 2.3.2.1 Magnus propagator

With  $\hat{M}$  being a general operator instead of the standard Hamiltonian  $\hat{H}$ , we can express the propagation of the coefficient matrix  $C(t)$  in a similar way as the propagation of wave functions in equation (2.3.16)

$$C(t) = U(t, t_0)C(t_0) = \exp\{-i(t - t_0)\hat{M}\}C(t_0). \quad (2.3.26)$$

By definition, the MAG2 propagator takes the second order ( $n = 1$ ) of the equation (2.3.15) and reads

$$\hat{U}_{MAG2}(t + \Delta t, t) = \exp\left\{-i\Delta t\hat{M}\left(t + \frac{\Delta t}{2}\right)\right\}. \quad (2.3.27)$$

Here the exponential midpoint rule is applied [76] and the propagator is defined at the middle of the interval  $[t + \Delta t, t]$ . Since  $\Delta t$  is usually tiny we can consider  $\hat{M}$  constant

inside this interval. By such construction, the midpoint remains the same as we propagate a state forward then backward in time and the time-reversibility is easily proven

$$\begin{aligned} \hat{U}_{MAG2}(t + \Delta t, t) \hat{U}_{MAG2}(t, t + \Delta t) \\ = \exp \left\{ -i\Delta t \hat{M}(t + \frac{\Delta t}{2}) \right\} \exp \left\{ i\Delta t \hat{M}(t + \frac{\Delta t}{2}) \right\} = \hat{I}. \end{aligned} \quad (2.3.28)$$

As explained in section 2.3.1, when not using the projectile basis we can work in an orthogonal basis. In this case, the operator inside the propagator is the standard Hamiltonian  $H$  which then becomes  $H'$  in the orthogonal basis (see equation (2.3.8)). This makes the propagator

$$\hat{U}_{MAG2}(t + \Delta t, t) = \exp \left\{ -i\Delta t \hat{H}'(t + \frac{\Delta t}{2}) \right\}. \quad (2.3.29)$$

Since  $H'$  is Hermitian, we can quickly show that the MAG2 propagator is unitary

$$U_{MAG2}^H U_{MAG2} = \exp \left\{ i\Delta t H'^H \right\} \exp \left\{ -i\Delta t H' \right\} = I. \quad (2.3.30)$$

Another advantage of operating in the orthogonal basis is the easy diagonalization of  $H'$  [72]

$$H' = A' E A'^H. \quad (2.3.31)$$

Introducing this expression into the propagator (2.3.29) simplifies the exponential term into a diagonal matrix thanks to the eigenvalue matrix  $E$

$$\exp \left\{ -i\Delta t H' \right\} = A' \exp \left\{ -i\Delta t E \right\} A'^H. \quad (2.3.32)$$

This gives us an exact evaluation of  $\hat{U}_{MAG2}$  and is only two approximations away from the general propagator in equation (2.3.15): the time discretization and the second-order expansion.

### 2.3.2.2 Crank-Nicolson propagator

The CN method, also known as the implicit midpoint rule is defined as [76]

$$\hat{U}_{CN}(t + \Delta t, t) = \left[ \hat{I} + \frac{i}{2} \Delta t \hat{M}(t + \frac{\Delta t}{2}) \right]^{-1} \left[ \hat{I} - \frac{i}{2} \Delta t \hat{M}(t + \frac{\Delta t}{2}) \right]. \quad (2.3.33)$$

Similar to  $\hat{U}_{MAG2}$  we can show that the CN propagator is time-reversible

$$\begin{aligned}
\hat{U}_{CN}(t + \Delta t, t) \hat{U}_{CN}(t, t + \Delta t) &= \left[ \hat{I} + \frac{i}{2} \Delta t \hat{M}(t + \frac{\Delta t}{2}) \right]^{-1} \left[ \hat{I} - \frac{i}{2} \Delta t \hat{M}(t + \frac{\Delta t}{2}) \right] \\
&\quad \left[ \hat{I} - \frac{i}{2} \Delta t \hat{M}(t + \frac{\Delta t}{2}) \right]^{-1} \left[ \hat{I} + \frac{i}{2} \Delta t \hat{M}(t + \frac{\Delta t}{2}) \right] \\
&= \left[ \hat{I} + \frac{i}{2} \Delta t \hat{M}(t + \frac{\Delta t}{2}) \right]^{-1} \left[ \hat{I} + \frac{i}{2} \Delta t \hat{M}(t + \frac{\Delta t}{2}) \right] = \hat{I}.
\end{aligned} \tag{2.3.34}$$

Recall our explanation concerning the unitarity of  $\hat{U}_{MAG2}$ , when the projectile basis is absent it is more practical to work in the orthogonal basis. Since the operator  $\hat{H}'$  is Hermitian,  $\hat{U}_{CN}$  can be proven unitary as follows

$$U_{CN}^H U_{CN} = B^H (A^H)^{-1} A^{-1} B = B^H (A A^H)^{-1} B = B^H B = I. \tag{2.3.35}$$

where

$$A = \hat{I} + \frac{i}{2} \Delta t \hat{H}', \quad B = \hat{I} - \frac{i}{2} \Delta t \hat{H}'. \tag{2.3.36}$$

What makes  $\hat{U}_{CN}$  less ideal than  $\hat{U}_{MAG2}$  is the extra approximations taken to transform the exponential term of equation (2.3.16) into expression (2.3.33). Let us start with the propagation from  $t$  to  $t + \Delta t$

$$\begin{aligned}
C(t + \Delta t) &\approx \exp\{-i\Delta t \hat{M}(t)\} C(t) \\
&\approx C(t) - i\Delta t \hat{M}(t) C(t) - \frac{1}{2} \Delta t^2 \hat{M}^2(t) C(t).
\end{aligned} \tag{2.3.37}$$

Here we have developed the exponential until the second order, which makes us equal to the number of approximations in  $\hat{U}_{MAG2}$ . Now using the time-reversibility we propagate from  $t$  to  $t - \Delta t$

$$\begin{aligned}
C(t - \Delta t) &\approx \exp\{i\Delta t \hat{M}(t)\} C(t) \\
&\approx C(t) + i\Delta t \hat{M}(t) C(t) - \frac{1}{2} \Delta t^2 \hat{M}^2(t) C(t).
\end{aligned} \tag{2.3.38}$$

Subtracting equation (2.3.38) from equation (2.3.37) leads to an expression with three instants

$$C(t + \Delta t) = C(t - \Delta t) - 2i\Delta t \hat{M}(t) C(t). \tag{2.3.39}$$

In order to reduce the above equation to only two instants, we add another approximation

$$C(t) \approx \frac{1}{2} \left( C(t + \Delta t) + C(t - \Delta t) \right). \quad (2.3.40)$$

Inserting equation (2.3.40) back into equation (2.3.39) gives us the CN propagator as seen in equation (2.3.33)

$$C(t + \Delta t) = \left[ \hat{I} + \frac{i}{2} \Delta t \hat{M} \right]^{-1} \left[ \hat{I} - \frac{i}{2} \Delta t \hat{M} \right] C(t) = \hat{U}_{CN}(t + \Delta t, t) C(t). \quad (2.3.41)$$

To reach this point we have employed at least one more approximation than the MAG2 propagator if we do not count the truncated exponential expansion used in the backward propagation. It has also been studied in reference [72] that the CN propagator is more sensitive to the time step  $\Delta t$  and more prone to produce numerical instability when  $\Delta t$  gets larger than 0.1 a.u. (2.4 as). Therefore for systems without projectile basis,  $\hat{U}_{MAG2}$  is preferred over  $\hat{U}_{CN}$ .

## 2.4 Random Electronic Stopping Power Calculations

This section aims to explain a few simplifications and techniques applied to acquire the random electronic stopping power (RESP). In a system of our interests composed of a projectile ion and a target atom, molecule or solid cluster, the total energy can be detailed as

$$E_{total} = E_e + E_{kin}^{proj} + E_{kin}^{targ}. \quad (2.4.1)$$

Here  $E_e$  is the electronic energy of the system,  $E_{kin}^{proj}$  the kinetic energy of the projectile nucleus and  $E_{kin}^{targ}$  the kinetic energy of the target nuclei. In a closed system,  $E_{total}$  stays constant during the entire simulation, therefore we can derive (2.4.1) by the projectile advancement  $x$  and write

$$0 = \frac{dE_e}{dx} + \frac{dE_{kin}^{proj}}{dx} + \frac{dE_{kin}^{targ}}{dx}. \quad (2.4.2)$$

Plugging this into (1.2.1) gives us

$$S(v) = \frac{dE_e}{dx} + \frac{dE_{kin}^{targ}}{dx}. \quad (2.4.3)$$

Now we can match these terms to those in (1.2.3) and get

$$S_e(v) = \frac{dE_e}{dx}, \quad (2.4.4)$$

$$S_n(v) = \frac{dE_{kin}^{targ}}{dx}. \quad (2.4.5)$$

We will now focus only on the electronic stopping power in equation (2.4.4) which is a generic expression. In practice for a given trajectory we will average the instant energy loss rate  $dE_e/dx$  over the entire travelled length  $L$  of the projectile [38][72][77]

$$S_e = \left\langle \frac{dE_e}{dx} \right\rangle = \frac{1}{L} \int_0^L dx \left( \frac{dE_e}{dx} \right). \quad (2.4.6)$$

An equivalent alternative to find the total stopping power is to average over time the retarding force  $\mathbf{F}_{proj}$  acting upon the projectile [65][56]

$$S = - \left\langle \mathbf{F}_{proj}(t) \cdot \frac{\mathbf{v}_{proj}(t)}{|\mathbf{v}_{proj}(t)|} \right\rangle. \quad (2.4.7)$$

with  $\mathbf{v}_{proj}$  being the projectile velocity. As mentioned earlier in section 2.2 about the basis choice, this second approach is more convenient for plane-wave basis simulations and would become extremely laborious using localized basis. Therefore only the first approach in equation (2.4.6) is adopted in MOLGW to calculate the electronic stopping power.

### 2.4.1 Simplification of Ehrenfest dynamics

The most accurate calculations of the ion-matter interactions require the use of Ehrenfest TDDFT dynamics. Due to the computational constraints, however, simplifications of these dynamics rules are often adapted. One common practice is to freeze all target nuclei positions so that  $E_{kin}^{targ} = 0$  and  $S_n = 0$  and equation (2.4.1) becomes [78]

$$E_{total} = E_e + E_{kin}^{proj}. \quad (2.4.8)$$

The second step is to assign a constant velocity to the projectile such that it travels in a straight line [79]. This means that  $E_{kin}^{proj}$  remains constant and when we derive  $E_{total}$  with respect to  $x$  we get

$$\frac{dE_{total}}{dx} = \frac{dE_e}{dx}, \quad (2.4.9)$$

and the electronic stopping power can now be expressed as

$$S_e = \left\langle \frac{dE_{total}(t)}{dx} \right\rangle = \frac{1}{v_{proj}} \left\langle \frac{dE_{total}(t)}{dt} \right\rangle. \quad (2.4.10)$$

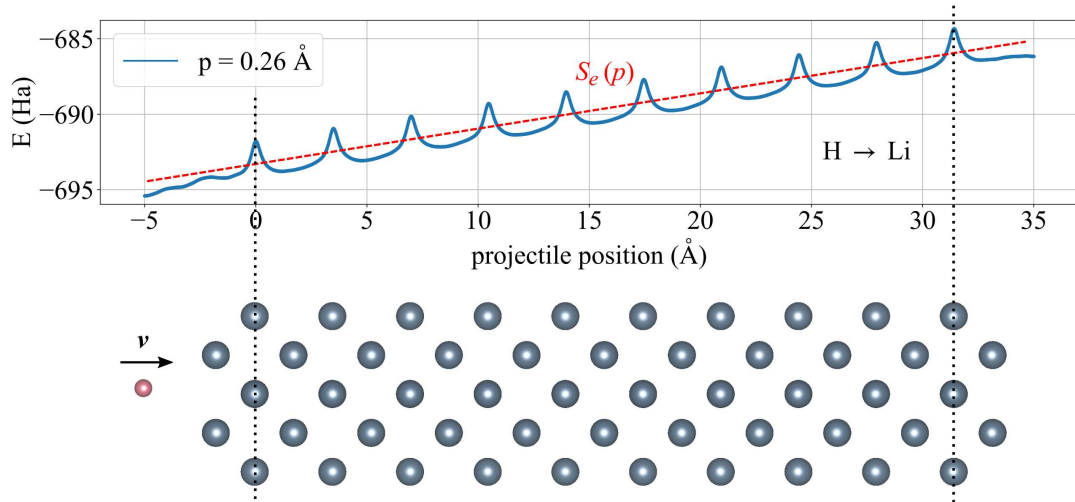
We can see that the system is no longer isolated and thus loses the energy conservation. However we have gained another conserved quantity which is the total amount of work done by the velocity constrain [38]

$$W = E_{total}(t) - \int dt \mathbf{F}_{proj}^v \cdot \mathbf{v}_{proj}. \quad (2.4.11)$$

The drag force  $\mathbf{F}_{proj}^v$  compensates the retarding force  $\mathbf{F}_{proj}$  on the projectile.

We would like to point out that these two simplifications on the target and the projectile nuclear motions are justifiable under the condition that the thickness of the simulated target is small enough so that the projectile velocity in a closed system would not vary significantly [38, 78]. In our study the largest thickness of a solid model does not exceed 10 nm which is 100 times thinner than samples used in experiments [80, 81, 82] and therefore more than safe to adopt the constraining measures on the nuclear motions.

Figure 2.4.1 demonstrates the energy evolution when hydrogen travels through a lithium cluster at a given trajectory. We observe that the total energy of the system increases overtime and peaks when the projectile encounters a target atom in close distance. If we average the slope of the energy curve, we obtain the single-trajectory stopping power  $S_e(p)$  by its definition in equation (2.4.10). We represent each single trajectory by the impact parameter  $p$  which is the projection of the target-projectile distance in the plane perpendicular to the projectile trajectory.



**Figure 2.4.1:** Energy profile of hydrogen (TZ) piercing through a cluster of 94 lithium atoms (CQZ/TZ/DZ) at impact parameter  $p = 0.26$  Å and  $v = 1.0$  a.u. (25 keV). The lower part illustrates the modeling system where the pink sphere represents the hydrogen atom and the blue spheres represent the lithium atoms. The upper panel describes the total energy variation with the blue solid line as a function of the projectile position. The averaged slope of the energy curve, represented by the red broken line, gives the single-trajectory stopping power  $S_e(p)$ .

## 2.4.2 Trajectory sampling and averaging

In real experiments the materials used are usually polycrystalline [83] and the projectile ion beam impinges the target at various impact parameters  $\mathbf{p}$  [72]. To better take into account of the experimental randomness, we employ what we call the ensemble average technique. First we sample multiple  $\mathbf{p}$  inside the elementary impact surface  $\mathcal{A}$  defined according to the symmetry of the crystal. Then at a given velocity  $v$  we calculate the single trajectory stopping power  $S_e(v, \mathbf{p})$  for all sampled  $\mathbf{p}$ . Finally we integrate  $S_e(v, \mathbf{p})$  over all  $\mathbf{p}$  and average over the impact surface  $\mathcal{A}$  to get the random electronic stopping power (RESP) related to  $v$

$$\langle S_e(v) \rangle = \frac{1}{\mathcal{A}} \int d\mathbf{p} S_e(v, \mathbf{p}). \quad (2.4.12)$$

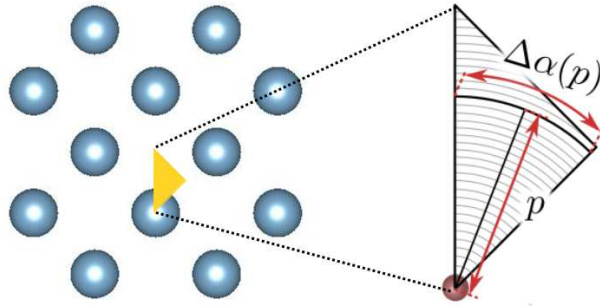
To avoid the sampling of a large number of random  $\mathbf{p}$ , a sampling technique is suggested by Maliyov *et al.* [48] to take advantage of the polar symmetry of  $\mathcal{A}$ . Figure 2.4.2 illustrates this method for the bcc aluminum at [001] orientation. It has also been intensively studied in reference [72] that the lithium and aluminum targets are only sensitive to the absolute value of impact parameters  $p$ . This allows us to reduce equation (2.4.12) into one dimension

and write

$$\langle S_e(v) \rangle = \frac{1}{\mathcal{A}} \int_0^{a_{lat}/2} dp \, p \Delta\alpha(p) S_e(v, p). \quad (2.4.13)$$

In the expression above, the arc  $p\Delta\alpha(p)$  is considered the geometric weight of the single-trajectory  $S_e(v, p)$  inside the impact surface and  $a_{lat}$  denotes the lattice constant. The determination of the angle  $\Delta\alpha(p)$  depends on the shape of the elementary surface  $\mathcal{A}$ . In the case of bcc [001] lithium and fcc [001] aluminum we have an isosceles right triangle impact surface and the angles  $\Delta\alpha(p)$  for the corresponding  $p$  are determined as

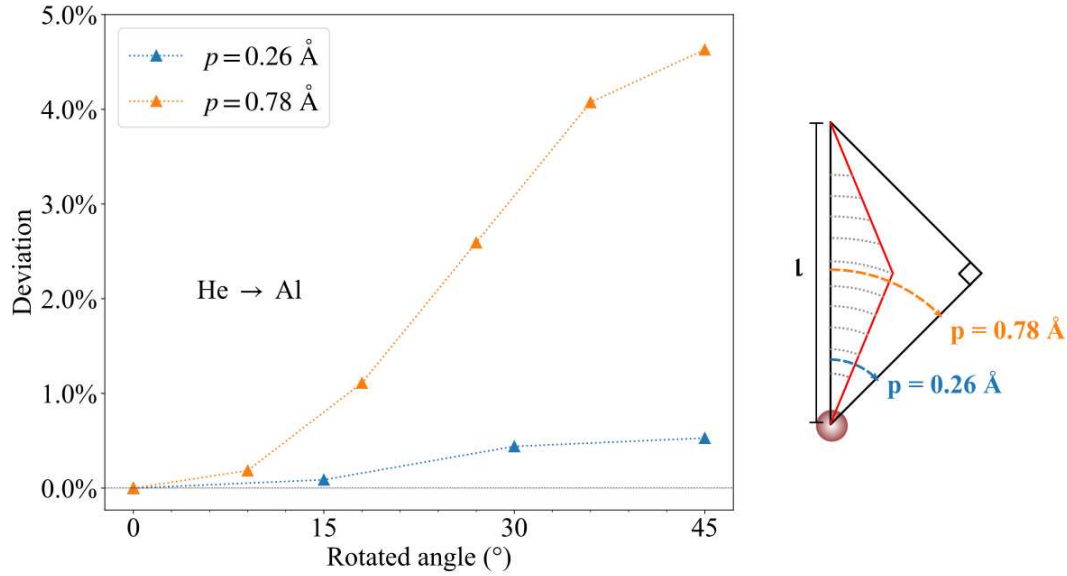
$$\Delta\alpha(p) = \begin{cases} \pi/4, & \text{if } 0 \leq p \leq \sqrt{2}a_{lat}/4, \\ 1/2 \arcsin(a_{lat}^2/4p^2 - 1), & \text{if } \sqrt{2}a_{lat}/4 < p \leq a_{lat}/2. \end{cases} \quad (2.4.14)$$



**Figure 2.4.2:** Polar symmetry sampling of impact parameters in fcc [001] aluminum. The left-side image shows the plane view of the target in perpendicular to the projectile trajectory. Each blue sphere represents an Al atom. The impact surface  $\mathcal{A}$  is represented by the yellow isosceles right triangle and is zoomed in at the right side of the figure. The red sphere in the zoomed image illustrates the atom from which we define  $\mathcal{A}$ . The absolute value  $p$  of the impact parameters as well as the matching angle  $\Delta\alpha(p)$  are highlighted with red double-headed arrows.

In order to further reduce errors caused by the angular dependence, we have improved the original sampling technique of Maliyov and coworkers [48]. The left part of figure 2.4.3 shows the angular error for two trajectories when rotating from the hypotenuse ( $0^\circ$ ) to one of the legs ( $45^\circ$ ) of the triangular impact surface featured in figure 2.4.2. Closer to the two base corners, less is the rotation range, thus the impact points that are most affected by the angular dependence are near the incenter where  $p_{inc} = \frac{\sqrt{2}}{2}l$ . In the case of aluminum the hypotenuse length is  $l = 1.43 \text{ \AA}$  and  $p_{inc} = 1.01 \text{ \AA}$ . This means that  $p = 0.78 \text{ \AA}$  is expected to be more sensitive to the angular change than  $p = 0.26 \text{ \AA}$ , which we can see in the figure 2.4.3. When compared to the stopping powers (SP) obtained at  $0^\circ$ , the results

increase with the rotation angle and at  $45^\circ$  the deviation is 0.5% for  $p = 0.26 \text{ \AA}$  and 4.5% for  $p = 0.78 \text{ \AA}$ . This has inspired us to take sampling points on the angle bisectors of the two base angles instead of along the hypotenuse. This new technique is demonstrated on the right side of figure 2.4.3 where the red lines indicate the sampling locations.



**Figure 2.4.3:** Angle induced errors for helium (DZ) impacting fcc [001] aluminum (CQZ/DZ/DZ) and the new sampling technique. On the left side, the deviations comparing to SP calculated at  $0^\circ$  rotation are displayed for two impact parameters: blue dotted line with markers represents errors for  $p = 0.26 \text{ \AA}$  and orange dotted line with markers represents errors for  $p = 0.78 \text{ \AA}$ . The right side of the figure illustrates the new sampling technique. The triangular impact surface takes its origin from the atom represented by a dark red sphere. The red solid lines indicate the angle bisectors of the base angles with the grey dotted lines indicating the rotation from the hypotenuse. To relate to the left-hand image of the figure, the rotations of the two impact parameters are illustrated with blue and orange dotted lines.

One special trajectory we would like to mention is the channeling condition. During experiments, one can use mono-crystal target at a specific orientation so that the projectile ends up traversing through a channel [84] without any head-on collisions into the target atoms or change of directions [38]. In the case of the impact surface in figure 2.4.2, the channeling point would be at the base corner opposite to the impacted atom. Typically this kind of setups gives very weak stopping power and some studies [85, 86] suggest that it is due to the relatively weak electron density inside the channels. Nevertheless the channeling condition provides a valuable way to study the stopping power since the experimental conditions are controlled and the simulations can be done with one single trajectory [38].

In this chapter we have reviewed some fundamental concepts about the DFT and TDDFT.

Then we have discussed about the matrix representations of several key mathematical terms inside a GTO basis set. When projectile basis is not used, matrix expressions become simpler in the orthogonal basis, and the second-order Magnus propagator is chosen over the Crank-Nicolson propagator. Some simplifications on the Ehrenfest dynamics and the sampling techniques employed to calculate the RESP are also presented. The next chapter reports a study carried out in parallel to this thesis. The stopping powers of proton and antiproton in LiF, simulated without projectile basis, are analyzed with unusual findings at low velocities.

## Chapter 3

# Electronic Stopping Power without Projectile Basis in LiF

This chapter is dedicated to a project where we have applied the no MB calculations previously developed by Maliyov *et al.* [48, 49, 72] to the proton and antiproton stopping power calculations in lithium fluoride (LiF) [46]. LiF is an insulator with a large band-gap of 13.6 eV [87]. Due to such an energy gap, when the projectile velocity is very low the kinetic energy of the projectile would be too weak to excite the target electrons. This leads to a threshold effect where the stopping power is zero until the projectile velocity passes a certain threshold value [88, 89, 90]. Historically there have been many debates over the existence of such a threshold effect in LiF. Although some groups of researchers have voiced their doubts against this phenomenon [91, 90], modern-day experiments have proven that a threshold indeed exists for proton stopping power in LiF [88, 92, 93].

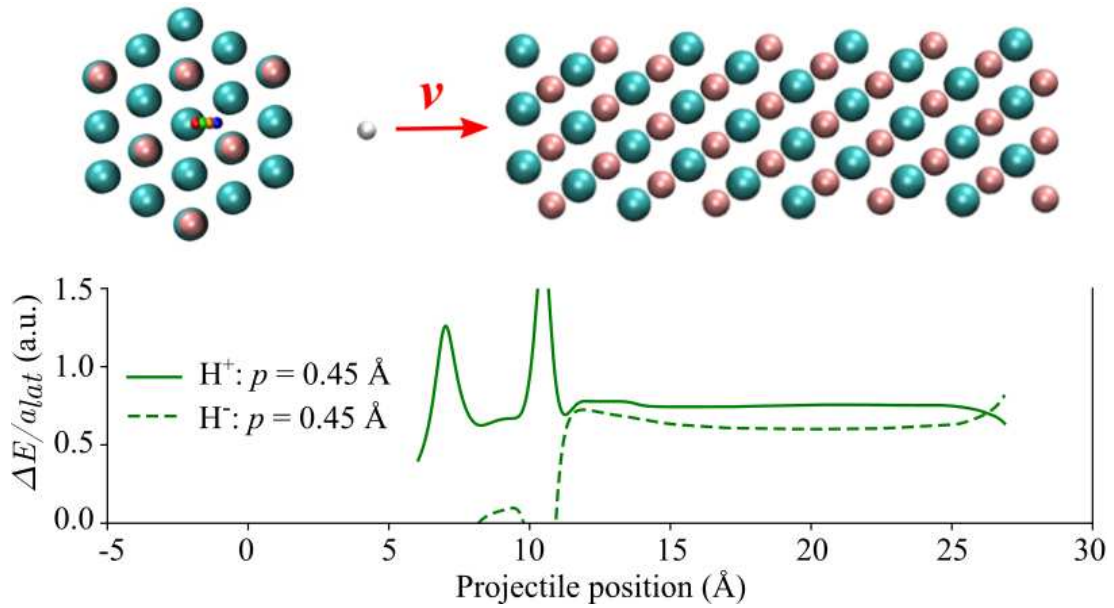
It is worth mentioning that in metallic materials there is no threshold effects at low velocities due to the absence of band gap, as we can see from the vast collections of experimental and theoretical studies in references [94, 95]. In addition, at low velocities the stopping powers in metals increase linearly [38] according to the formula developed in reference [96] which is similar to the Fermi and Teller's formula [41] in equation (1.2.5).

In the following discussions we will start by looking at the RESP of proton and antiproton in LiF. Experimental data and several groups of simulated results are compared to highlight the stopping power threshold of proton and the positive and negative Barkas effects. Then we will move on to a couple of analysis that have identified the cause of the newly reported negative Barkas effect. The influence of the projectile charge sign is analyzed

through applying fractional charges between -1 and 1, and the projectile's interactions with individual  $\text{Li}^+$  and  $\text{F}^-$  ions are investigated by isolated ions study.

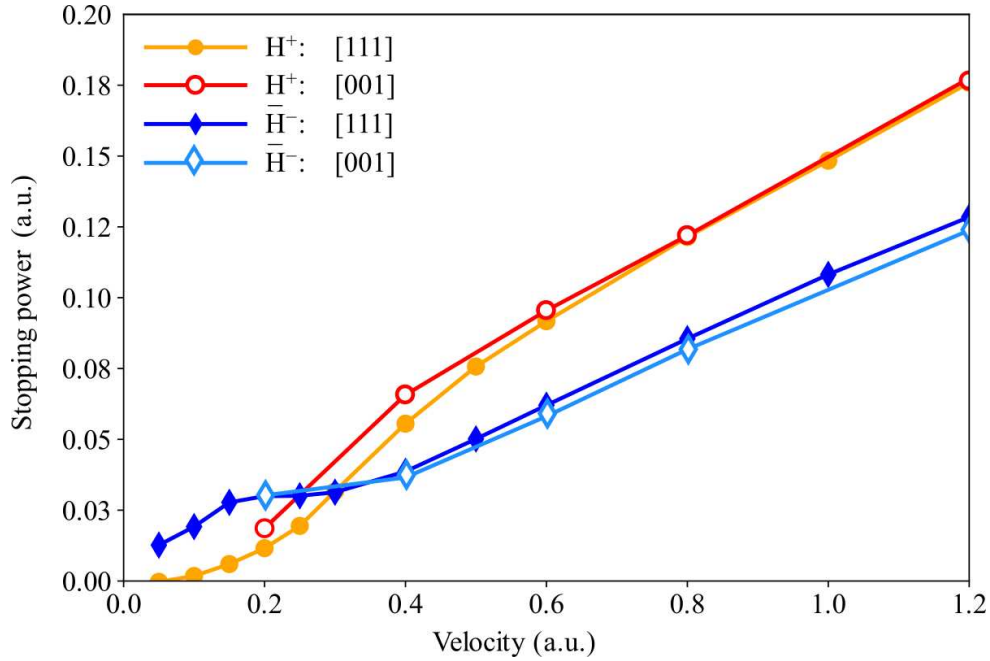
### 3.1 Stopping Powers of Proton and Antiproton in LiF

The crystal structure of LiF studied is the rocksalt. After some careful convergence tests on the geometry similar to those presented in section 5.1, we have decided to use a LiF cluster of 126 atoms that is 22 Å in length and 6 Å in diameter. The center of the cluster is on the column of atoms closest to the projectile track and the cluster is oriented at [111] direction. Different views of the LiF cluster is illustrated in figure 3.1.1, as well as an example of the running stopping power  $[E(z + a_{\text{lat}}) - E(z)]/a_{\text{lat}} = \Delta E/a_{\text{lat}}$  of proton and antiproton for a single trajectory. With the entrance to the cluster placed at  $z = 0$  Å, the stable  $\Delta E/a_{\text{lat}}$  after 15 Å inside the cluster proves the length to be sufficient.



**Figure 3.1.1:** Transversal and longitudinal views of LiF [111] (upper panel) and the running stopping power  $\Delta E/a_{\text{lat}}$  of proton in LiF (lower panel) [46]. The spheres in cyan, pink, and white represent respectively the atoms of lithium, fluorine, and the projectile. In the transversal view of LiF, the smaller spheres in red, green, orange, and blue represent the four impact parameters  $p$  used in this study. Discussions about the number of impact parameters can be found in the Supplementary Material of reference [46]. The running SP at  $p = 0.45$  Å is reported for both proton (green solid line) and antiproton (green dashed line) projectiles as a function of projectile position at  $v = 0.4$  a.u..

The choice of the crystal orientation in a cubic structure such as the rocksalt has been observed to be of little influence over the RESP by the work of Maliyov [72]. We support his observation by comparing the proton and antiproton RESP in LiF calculated at both [111] and [001] directions in figure 3.1.2. It is obvious to see that for each projectile the results are almost identical between the two cluster orientations. Details of other convergence tests concerning the radius, the number of impact parameters and the exchange-correlation functions are reported in the Supplementary Material of reference [46].

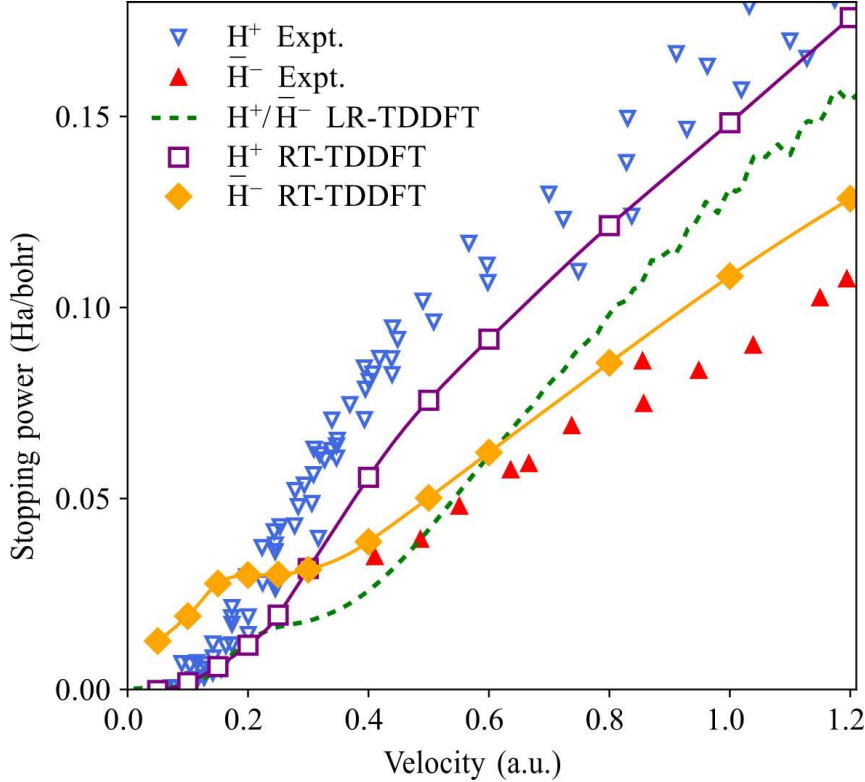


**Figure 3.1.2:** Crystal orientation sensitivity of the RESP of proton and antiproton in LiF [46]. The orange line with full circles plots the proton RESP with [111] cluster direction. The red line with empty circles plots the proton RESP obtained at [001]. The dark blue line with full diamonds plots the antiproton RESP at [111] and the light blue line with empty diamonds plots the antiproton RESP at [001].

The target basis used is a mixture of ACQZ/DZ/DZ where the 48 atoms closest to the projectile trajectory are described with the ACQZ basis set. This choice is made independently of the target basis convergence test in section 5.1.3 and we have not verified whether the ACQZ basis can be replaced by the lighter CQZ basis like in the case of aluminum to save computational efforts. The main goal here is to use a basis set as complete as possible within our resource limits.

Several sets of proton and antiproton RESP are presented in figure 3.1.3 including the experimental data [92, 93, 90], the linear-response (LR) TDDFT results calculated with ABINIT [97, 44] and our real-time (RT) TDDFT results from MOLGW [46]. Let

us first focus on the proton. The rich number of experimental data at very low velocities  $v \leq 0.2$  a.u. (1 keV) gives clear evidences of a threshold around  $v = 0.05$  a.u. (60 eV). Before this point the RESP of proton in LiF is zero. While this effect is well captured by the LR calculations, the LR curve is completely off the track of the experimental data after  $v = 0.2$  a.u.. Our RT results on the other hand do not only describe correctly the threshold effect but also follow closely the evolution of the experimental data at higher velocities.



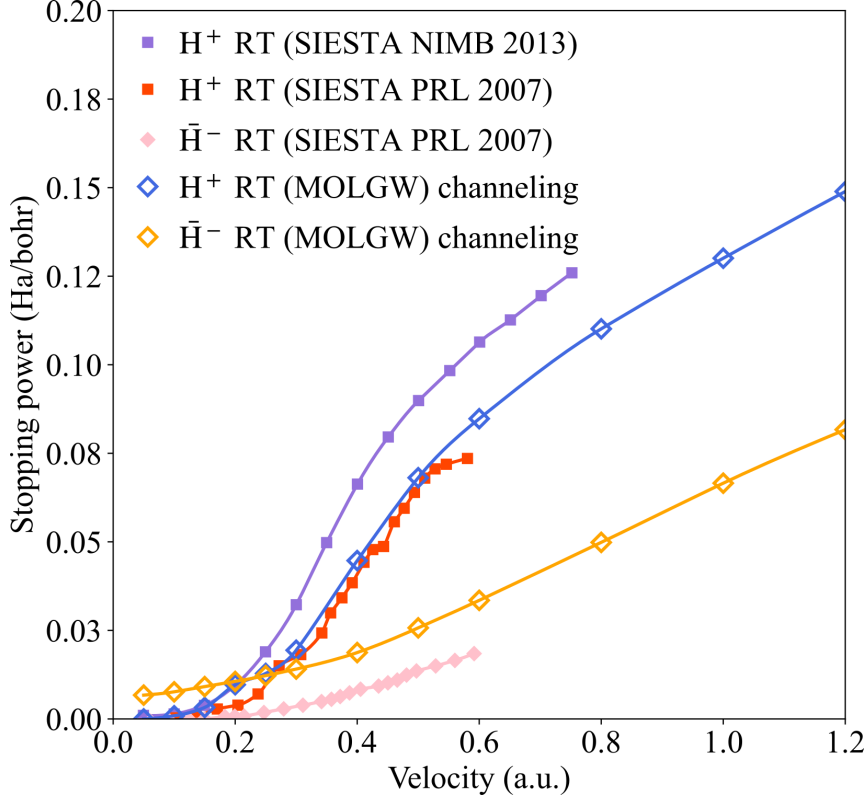
**Figure 3.1.3:** RESP of proton and antiproton in LiF. The blue and red triangles reports the collections of experimental findings [92, 93, 90] for proton and antiproton respectively. The green broken line plots the results from the linear-response (LR) TDDFT calculations which is insensitive to the charge sign of the projectile. Our real-time (RT) TDDFT results [46] are represented by lines with diamonds: the purple line plots for proton and the orange line for antiproton.

Now we switch our attention to the antiproton. At low velocities the experimental records are scarce and we have only found data starting from  $v = 0.3$  a.u. (2 keV). According to the experiments the antiproton RESP is significantly lower than that of the proton. This phenomenon where the stopping power of a negative pion is inferior to that of a positive pion has been first confirmed by Barkas and co-workers [45] and is therefore named the Barkas effect. The LR methods cannot capture this effect due to the quadratic dependence on the projectile charge  $Z$  in equation (1.2.6) and gives very different results

from the experiments. Corrections to the Lindhard LR formula then involve a polynomial expansion into the cubic term  $Z^3$  [36]. The RT calculations go beyond this charge sign limit of the LR approach and predict correctly the Barkas effect between the proton and antiproton RESP for  $v \geq 0.3$  a.u.. In addition the accordance is very good between the RT and the experimental data.

The surprising observations of the RT results take place below  $v = 0.3$  a.u. where the RESP of antiproton becomes superior to that of proton. Since this behavior is the opposite of the common Barkas effect, we decide to call it the negative Barkas effect and refer to the former as the positive Barkas effect. At the same time, apart from a narrow platform between  $v = 0.1$  (250 eV) and 0.3 a.u. the RT curve does not show any sign of threshold for the antiproton stopping power at lower velocities, which is a major difference from the proton RESP.

There are two other valuable references to compare our RT-TDDFT findings with. Previously, the research teams of Pruneda [79] and Zeb [86] have conducted the RT-TDDFT studies of proton and antiproton stopping power in LiF using SIESTA [98, 66, 99]. Instead of taking multiple random trajectories, their simulations are set in either a [110] or [001] channel. While they have correctly captured the proton threshold and the positive Barkas effect, they also report a threshold velocity for antiproton and have shown no signs of negative Barkas effect. In figure 3.1.4 we present the channeling SP results from both SIESTA and MOLGW.



**Figure 3.1.4:** Channeling SP of proton and antiproton in LiF calculated by both SIESTA [79, 86] and MOLGW [46]. Results from reference [86] concern only the proton and is plotted by a purple line with squares. Results from reference [79] report for both the proton and the antiproton and are plotted by a red line with squares then a pink line with diamonds. Our MOLGW calculations use a blue line with diamonds for the proton and a yellow line with diamonds for the antiproton.

For proton, results from reference [86] have higher values than our MOLGW findings starting from  $v = 0.2$  a.u., while results from reference [79] are almost identical to ours. The agreement in the overall trend among these three sets of calculations is pretty good. Although both references [79] and [86] use the same software SIESTA, the discrepancy in their results is caused by the differences in their modeling parameters.

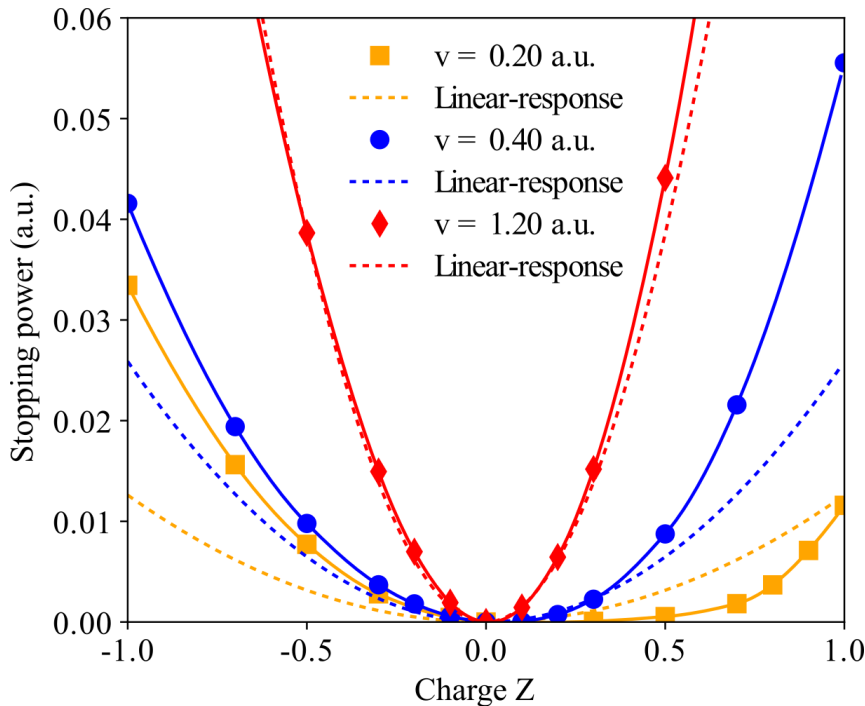
For antiproton, the overall trend of MOLGW calculations is in perfect agreement with the results of Pruneda *et al.* [79], with only a small difference in the absolute values. Comparing with the RESP of antiproton in figure 3.1.3, we can see the importance of including random trajectories at low velocities to capture the negative Barkas effect.

In this section we have talked about the proven threshold of the proton stopping power in LiF as well as the positive and negative Barkas effects between the proton and antiproton stopping powers. With our MOLGW random-trajectory calculations we have captured all of these phenomena. While other RT-TDDFT calculations from SIESTA [79, 86] also describe

correctly the behaviors of the proton stopping power, their channeling approach might have prevented them from observing the unusual trend of antiproton SP at low velocities. To our knowledge, the negative Barkas effect that we have predicted is unprecedented and in the following sections we will try to explain the origin of such a phenomenon.

## 3.2 Fractional charges analysis

The idea behind this analysis is to gradually change the projectile charge state  $Z$  from 1 (proton) to -1 (antiproton) and observe how the RESP in LiF is affected. The in-between charge states would therefore be fractional and the resulting stopping powers are reported in figure 3.2.1 at three different velocities  $v = 0.2, 0.4$  and  $1.2$  a.u.. Besides the RT-TDDFT calculations, we have also run the LR-TDDFT simulations at the same conditions. By construction, due to the  $Z^2$  dependency the linear-response results give a symmetric parabolic trend as the charge  $Z$  goes towards the positive and the negative ends. This is a good reference to compare with the RT studies to evaluate the asymmetry in the charge behaviors.

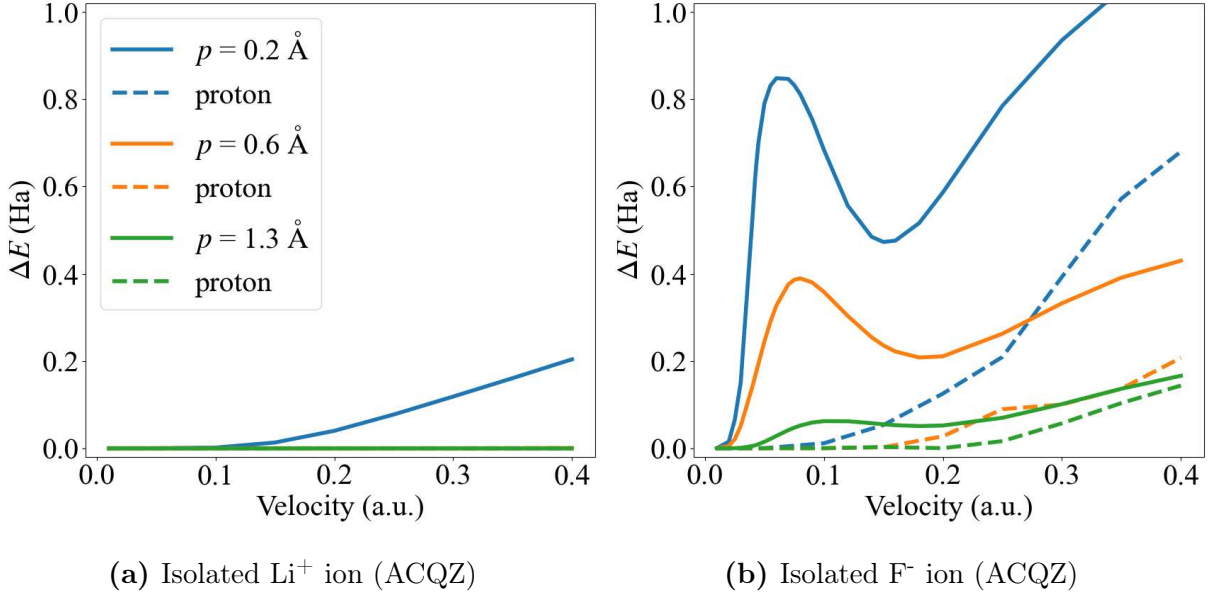


**Figure 3.2.1:** Fractional charges analysis of RESP in LiF with the projectile charge  $Z$  varying between -1 and 1 [46]. Three velocities are studied and their results marked with different colours:  $v = 0.2$  a.u. in orange,  $v = 0.4$  a.u. in blue and  $v = 1.2$  a.u. in red. Results from the RT-TDDFT calculations are reported by solid lines with markers, whereas results obtained by the LR-TDDFT methods are plotted by dashed lines.

We can see from figure 3.2.1 that at a high enough velocity,  $v = 1.2$  a.u., the RT curve is almost identical to the LR curve. As the velocity decreases, the RT curve starts to lose its symmetry. At  $v = 0.4$  a.u., a positive Barkas effect can be observed where the RESP of positive charges are greater than those of negative charges, especially when  $|Z|$  is close to 1. Finally at  $v = 0.2$  a.u., the RT curve is completely asymmetrical and the RESP of positive charges all become inferior to those of the opposite sign. This is thus the negative Barkas effect and is consistent with that observed between the proton and antiproton in figure 3.1.3. We will now investigate further into the nature of this effect by studying the influence of these two projectiles on the two ions composing LiF:  $\text{Li}^+$  and  $\text{F}^-$ .

### 3.3 Isolated ions analysis

The first step of the investigation on isolated ions of LiF is to run the RT-TDDFT stopping power simulations in diatomic systems built with a projectile and an isolated ion. There are four pairs of particles to be considered: 1) proton +  $\text{Li}^+$ ; 2) antiproton +  $\text{Li}^+$ ; 3) proton +  $\text{F}^-$ ; 4) antiproton +  $\text{F}^-$ . The principle of these calculations are the same as that used for the diatomic systems described in section 4.2, only without projectile basis. We report in figure 3.3.1 the total energy variation  $\Delta E$  before and after impacting the target ion at slow velocities  $v \leq 0.4$  a.u. (4 keV). This specific velocity zone is chosen to focus on the range where the negative Barkas effect happens. These results are calculated with different impact parameters  $p$  to determine the dependency of the negative Barkas effect on the trajectory.



**Figure 3.3.1:** Energy variation  $\Delta E$  of proton and antiproton in isolated  $\text{Li}^+$  (left-side image) and  $\text{F}^-$  ions (right-side image). Three impact parameters  $p = 0.2, 0.6, 1.3 \text{ \AA}$  are studied and marked with colors blue, orange and green respectively. Results for the proton projectile are plotted with dashed lines whereas results for the antiproton with solid lines.

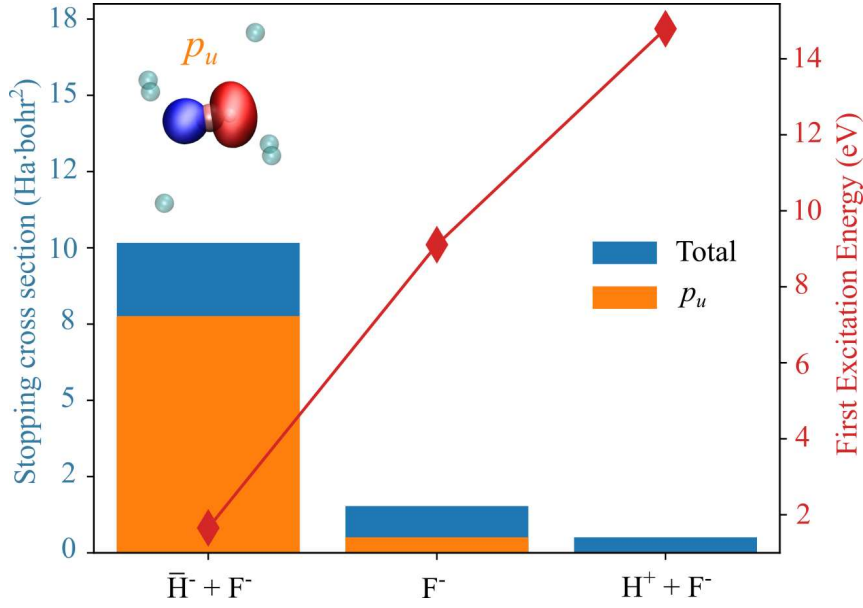
With  $\Delta E$  shown at the same scale in both images in figure 3.3.1, it is obvious to see that  $\text{F}^-$  is more impacted by the two projectiles than  $\text{Li}^+$ . Both target ions interact more strongly with the antiproton than with the proton, but this difference between the two projectiles diminishes as  $v$  and  $p$  rise in value. In the case of  $\text{Li}^+$ , the interactions with proton is too weak to be visible at the chosen scale in figure 3.3.1a. Focusing on the antiproton results, we observe for  $\text{F}^-$  a much more complex dependency of  $\Delta E$  on the velocity below  $v = 0.2 \text{ a.u.}$  (1 keV) than for  $\text{Li}^+$ . Not only does it have great magnitude, it also possesses a peak around  $v = 0.1 \text{ a.u.}$  (250 eV). Based on the above observations we conclude that, between the two ions of LiF,  $\text{F}^-$  is the major contributor to the negative Barkas effect. The next step is therefore to analyze the electronic structure of  $\text{F}^-$  to identify the main factors that cause this effect.

For this analysis, we have turned to the linear-response TDDFT calculations in MOLGW since it can give practical insights about the excitation energies and the contributions from each orbital to the stopping power. As the target is an isolated ion instead of a material with certain thickness, it makes more sense to measure the stopping cross section (SCS) instead of the stopping power [36]

$$S_{cs} = S/\rho_T, \quad (3.3.1)$$

where  $S_{cs}$  is the stopping cross section,  $S$  is the stopping power and  $\rho_T$  is the density of

the target.

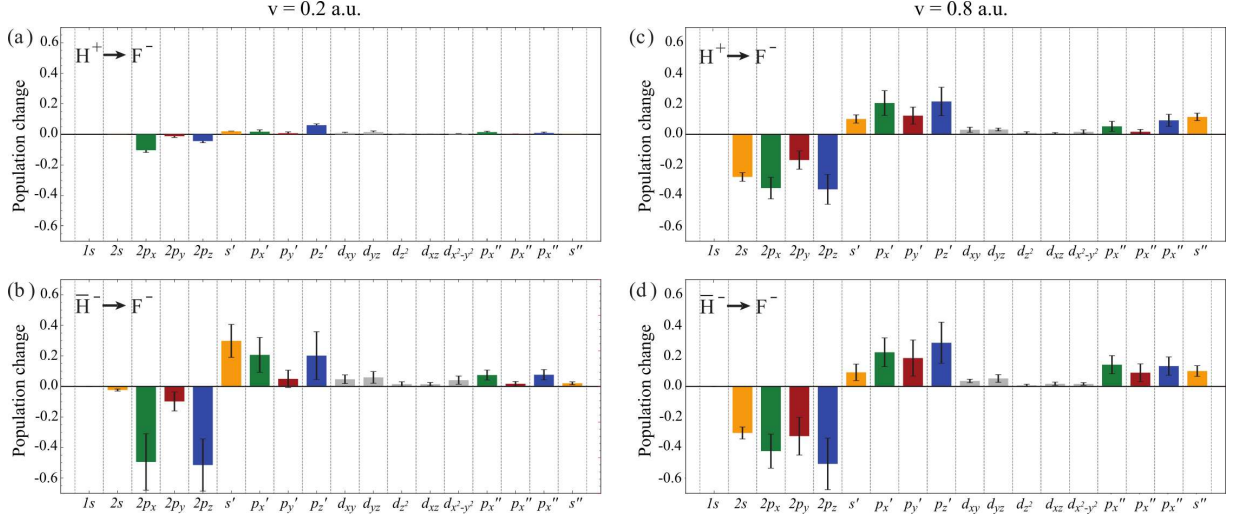


**Figure 3.3.2:** Stopping cross section (SCS) (bars) and the first excitation energy  $E_1$  (diamonds) in three systems of isolated  $F^-$  ion (from left to right): 1) antiproton +  $F^-$ ; 2)  $F^-$  alone; 3) proton +  $F^-$ . The left y-axis measures the SCS of the three systems and the right y-axis measures the  $E_1$ . The total SCS of each system is represented by a blue bar and the contributions from the  $F^-$  orbital  $p_u$  by an orange bar. The  $E_1$  values of the three systems are marked by red diamonds and linked together by a red line.

In figure 3.3.2 we present both the SCS and the first excitation energy  $E_1$  for three systems: 1) antiproton +  $F^-$ ; 2)  $F^-$  alone; 3) proton +  $F^-$ . The velocity that we are interested in is  $v = 0.2$  a.u. at which the negative Barkas effect is well pronounced in figure 3.1.3. We have also chosen to work with the impact parameter  $p = 0.45$  Å that is close enough to the target according to figure 3.3.1 and has a good statistic probability inside the impact zone (see the notion of geometric weight in section 2.3.2). For the SCS both the total value and the major contribution from one specific  $F^-$  orbital  $p_u$  are reported.

Looking first at the total SCS, we can quickly notice it to be the highest in the presence of antiproton and the lowest in the presence of proton. This is expected knowing the RESP of antiproton to be higher than that of proton in figure 3.1.3 at this velocity. Moving on to the first excitation energy we see that logically a lower total  $E_1$  is associated with a higher SCS like in the case of the antiproton. Meanwhile in the presence of proton the  $E_1$  value is extremely high, indicating a very stable system. Coming back to the orbital details of SCS we notice that the major contribution comes from one particular  $p_u$  orbital of the  $F^-$  ion, which is severely destabilized by the antiproton. The subscript  $u$  denotes the unit vector that points from  $F^-$  towards the the projectile. We believe that it is due to

the destabilization of this orbital that the RESP of antiproton is unusually high at low velocities. In contrast with the very stable system formed by  $F^-$  and the proton, the easy excitation of the  $F^-$  ion by the antiproton finally leads to the negative Barkas effect.



**Figure 3.3.3:** Electron population change of the  $F^-$  orbitals [46]. Since only  $1s2s2p$  are occupied in  $F^-$ , virtual orbitals with higher quantum numbers are labeled without their quantum numbers. Image (a) describes the orbital population change in the presence of proton at  $v = 0.2$  a.u. and image (b) describes the change in the presence of antiproton. Images (c) and (d) report for systems at  $v = 0.8$  a.u. (16 keV), with proton and antiproton projectile respectively.

At last, to further prove the  $F^-$  orbital destabilization as a unique feature in the presence of antiproton at low velocities, we have mapped out the  $F^-$  orbital population change in figure 3.3.3 using RT-TDDFT methods for both proton and antiproton projectiles at two different velocities. The impact parameters are chosen along the  $y$ -axis, whereas the trajectories are along the  $z$ -axis. The population  $p_i$  of a ground-state ( $t_0$ ) orbital  $i$  is initially

$$p_i(t_0) = \sum_j f_j |\langle \psi_i(t_0) | \psi_j(t_0) \rangle|^2 = f_i, \quad (3.3.2)$$

due to the orthonormality of wave functions. Here  $f_i$  and  $f_j$  are the occupation numbers of orbitals  $i$  and  $j$ . At a later instant  $t$  the population becomes

$$p_i(t) = \sum_j f_j |\langle \psi_i(t_0) | \psi_j(t) \rangle|^2, \quad (3.3.3)$$

The change in population of a single orbital  $i$  can thus be expressed as

$$\Delta p_i = p_i(t) - p_i(t_0) = \sum_j f_j |\langle \psi_i(t_0) | \psi_j(t) \rangle|^2 - f_i. \quad (3.3.4)$$

At  $v = 0.2$  a.u. there is almost no orbital excitations at the presence of proton, whereas at the presence of antiproton the  $2p$  orbitals as well as some higher level  $s$  and  $p$  orbitals are noticeably excited. Since the projectiles move in the  $xz$  plane, orbitals  $p_x$  and  $p_z$  are far more affected than the orbital  $p_y$  which is perpendicular to the plane. This directional difference of the excited  $p$  orbitals agrees with the LR study where the orbital pointing from  $F^-$  towards the projectile is observed to be destabilized. On the other hand, once the velocity is high enough, as in the case of  $v = 0.8$  a.u., the orbital excitations are no longer unique to the system with antiproton projectile and the negative Barkas effect vanishes.

Summing up this chapter, we have first presented the RESP of proton and antiproton in LiF where an unprecedented negative Barkas effect is observed thanks to our RT-TDDFT calculations. Then we have found a plausible explanation of this phenomenon through two major analysis. One is the study of fractional charges where we explore the evolution of RESP as the projectile charge goes gradually from  $Z = -1$  to 1. This confirms the appearance of the negative Barkas effect at low velocities as  $Z$  approaches -1. The second study looks at the isolated ions of LiF, notably  $F^-$  who is the most affected by the presence of antiproton due to the destabilization of its  $p$  orbitals. We believe that it is due to this  $F^-$  orbital destabilization which is unique to the antiproton projectile at low velocities that the negative Barkas effect takes place in LiF.

Here we come to the end of simulations without projectile basis. The next chapter will focus on the changes and adaptations in theoretical formulas and propagators due to the moving projectile basis.

# Chapter 4

## Adapting Equations with Moving Projectile Basis

This chapter is dedicated to the theoretical explanation of the difference between modeling a bare projectile and a projectile with basis functions. We will start by demonstrating how the addition of projectile basis introduces position dependency into the time-dependent equations. The time-evolution of the basis set induces a time-dependent Hilbert space, which translates in an extra operator  $\hat{D}$  that possesses a special matrix form and important physical properties. Then some numerical findings are provided to better illustrate these properties. The second half of this chapter discusses how the second-order Magnus (MAG2) propagator and the Crank-Nicolson (CN) propagator are modified with respect to the moving projectile basis. We will explain that while the former presents many advantages in systems without projectile basis, the latter is more suitable when projectile basis is applied.

### 4.1 Projectile Position Dependency

While adding basis on the projectile allows the latter to carry electrons, special treatments are required to take into account of the projectile electron displacements when transitioning from the ground state to the propagated states. At the ground state everything is static so there is no need to define a reference frame for movements. However, to debut the propagation where an ion is in continuous movement, it is instructive to establish the link between the laboratory frame  $F_o$  and the frame  $F_v$  centered on the moving ion. In the

following sections we will demonstrate through time-dependent equations that the change of reference frame brings a phase factor to the wave functions. The addition of this phase factor is avoidable by introducing a gradient operator  $\hat{D}$  in the time-dependent equations. The properties and numerical studies of  $\hat{D}$  will be discussed afterwards. We temporarily adopt the SI units in this section for a more insightful equation development.

### 4.1.1 Change of reference frames

The change between inertial reference frames entails Galilean transformations [100]. Fortunately, the TDSE is invariant under the space-time symmetry transformation for two frames of reference  $F_o$  and  $F_v$  moving at constant velocity  $\mathbf{v}$  relative to each other [100]. Since we use rectilinear trajectories for the projectile and that its velocity is defined along a single axis, the  $x$ -axis for example, the following demonstrations will be one-dimensional. Under this setting, the position and the time in both frames have the following relations

$$\begin{aligned} x_o &= x_v + vt_v, \\ t_o &= t_v. \end{aligned} \tag{4.1.1}$$

In either frame the density probability should be the same,

$$|\Psi_o(x_o, t_o)|^2 = |\Psi_v(x_v, t_v)|^2 \tag{4.1.2}$$

and therefore the wave functions  $\Psi_o$  and  $\Psi_v$  differ only by a phase factor called the electron translation factor (ETF)

$$\Psi_o(x_o, t_o) = e^{if(x_o, t_o)} \Psi_v(x_v, t_v). \tag{4.1.3}$$

We can obtain the expression for the function  $f(x_o, t_o)$  by finding the relation between the two frames. For a more generalized discussion, we will go back to the standard TDSE which in the frame  $F_v$  has the form

$$i\hbar \frac{\partial}{\partial t_v} \Psi_v(x_v, t_v) = \left[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x_v^2} + W_v(x_v) \right] \Psi_v(x_v, t_v), \tag{4.1.4}$$

Here we have grouped all potential operators from (2.1.2) into one single term  $W$  to simplify the writing. The potential energy in both frames are equivalent [100][51],

$$W_v(x_v) = W_o(x_o), \quad (4.1.5)$$

and the differential operators transform as

$$\begin{aligned} \frac{\partial}{\partial x_v} &= \frac{\partial}{\partial x_o} \\ \frac{\partial}{\partial t_v} &= \frac{\partial}{\partial t_o} + v \cdot \frac{\partial}{\partial x_o}. \end{aligned} \quad (4.1.6)$$

Substituting (4.1.3), (4.1.5) and (4.1.6) into (4.1.4) gives

$$\begin{aligned} -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x_o^2} \Psi_o + W_o(x_o) \Psi_o + i\hbar \left[ \frac{\hbar}{m} \frac{\partial f}{\partial x_o} - v \right] \frac{\partial \Psi_o}{\partial x_o} \\ + \left[ \frac{i\hbar^2}{2m} \frac{\partial^2 f}{\partial x_o^2} + \frac{\hbar^2}{2m} \left( \frac{\partial f}{\partial x_o} \right)^2 - \hbar v \cdot \frac{\partial f}{\partial x_o} - \hbar \frac{\partial f}{\partial t_o} \right] \Psi_o = i\hbar \frac{\partial \Psi_o}{\partial t_o}. \end{aligned} \quad (4.1.7)$$

Eventually we want to reduce this long equation into the usual TDSE in  $F_o$

$$i\hbar \frac{\partial}{\partial t_o} \Psi_o(x_o, t_o) = \left[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x_o^2} + W_o(x_o) \right] \Psi_o(x_o, t_o). \quad (4.1.8)$$

In order to eliminate all extra terms, the function  $f(x_o, t_o)$  has to fulfill the following conditions

$$\frac{\hbar}{m} \frac{\partial f}{\partial x_o} - v = 0, \quad (4.1.9a)$$

$$\frac{\partial^2 f}{\partial x_o^2} = 0, \quad (4.1.9b)$$

$$\frac{\hbar}{2m} \left( \frac{\partial f}{\partial x_o} \right)^2 - v \cdot \frac{\partial f}{\partial x_o} - \frac{\partial f}{\partial t_o} = 0. \quad (4.1.9c)$$

The second expression (4.1.9b) results from the spatial derivative of equation (4.1.9a). Putting it back to equation (4.1.7) then gives us the condition (4.1.9c). Based on these constraints, we can finally construct a real function

$$f(x_o, t_o) = \frac{m}{\hbar} \left( v \cdot x_o - \frac{1}{2} v^2 t_o \right). \quad (4.1.10)$$

Now we will prove how the application of ETF with the basis expansion leads to equivalent expressions in both frames. Let us first rewrite (4.1.3)

$$\sum_i \sum_\alpha C_{\alpha i}^o(t_o) \phi_\alpha^o(x_o) = e^{i\frac{m}{\hbar}(v \cdot x_o - \frac{1}{2}v^2 t_o)} \sum_i \sum_\alpha C_{\alpha i}^v(t_v) \phi_\alpha^v(x_v). \quad (4.1.11)$$

The unicity of basis expansion implies an element-to-element equality [50] which allows us to write

$$e^{-i\frac{m}{\hbar}(\mathbf{v} \cdot \mathbf{r}_o - \frac{1}{2}\mathbf{v}^2 t_o)} C_{\alpha i}^o(t_o) \phi_\alpha^o(x_o) = C_{\alpha i}^v(t_v) \phi_\alpha^v(x_v). \quad (4.1.12)$$

The standard TDSE in frame  $F_v$  expands as

$$\begin{aligned} i\hbar \frac{\partial}{\partial t_v} \left( \sum_\alpha C_{\alpha i}^v(t_v) \phi_\alpha^v(x_v) \right) \\ = \left[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x_v^2} + W_v(x_v) \right] \sum_\alpha C_{\alpha i}^v(t_v) \phi_\alpha^v(x_v). \end{aligned} \quad (4.1.13)$$

Switching into the laboratory frame  $F_o$  using relations (4.1.5), (4.1.6) and (4.1.12) gives us

$$\begin{aligned} i\hbar \left[ \frac{\partial}{\partial t_o} + v \cdot \frac{\partial}{\partial x_o} \right] \left( e^{-i\frac{m}{\hbar}(v \cdot x_o - \frac{1}{2}v^2 t_o)} \sum_\alpha C_{\alpha i}^o(t_o) \phi_\alpha^o(x_o) \right) \\ = \left[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x_o^2} + W_o(x_o) \right] e^{-i\frac{m}{\hbar}(v \cdot x_o - \frac{1}{2}v^2 t_o)} \sum_\alpha C_{\alpha i}^o(t_o) \phi_\alpha^o(x_o). \end{aligned} \quad (4.1.14)$$

The development of the left-hand side of this equation leads to

$$\begin{aligned} i\hbar \left[ \frac{\partial}{\partial t_o} + v \cdot \frac{\partial}{\partial x_o} \right] \left( e^{-if} \sum_\alpha C_{\alpha i}^o(t_o) \phi_\alpha^o(x_o) \right) \\ = i\hbar e^{-if} \sum_\alpha \left[ \frac{\partial}{\partial t_o} C_{\alpha i}^o(t_o) + C_{\alpha i}^o(t_o) v \cdot \frac{\partial}{\partial x_o} \right] \phi_\alpha^o(x_o) \\ + \frac{mv^2}{2} e^{-if} \sum_\alpha C_{\alpha i}^o(t_o) \phi_\alpha^o(x_o). \end{aligned} \quad (4.1.15)$$

At the same time the right-hand side develops into

$$\begin{aligned}
\left[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x_o^2} + W(x_o) \right] e^{-if} \sum_{\alpha} C_{\alpha i}^o(t_o) \phi_{\alpha}^o(x_o) \\
= e^{-if} \sum_{\alpha} C_{\alpha i}^o(t_o) \left[ -\frac{\hbar^2}{2m} \nabla_{x_o}^2 + W(x_o) \right] \phi_{\alpha}^o(x_o) \\
+ \frac{mv^2}{2} e^{-if} \sum_{\alpha} C_{\alpha i}^o(t_o) \phi_{\alpha}^o(x_o) \\
+ i\hbar e^{-if} \sum_{\alpha} C_{\alpha i}^o(t_o) v \cdot \frac{\partial}{\partial x_o} \phi_{\alpha}^o(x_o).
\end{aligned} \tag{4.1.16}$$

Equalizing both sides gives us the final expression of TDSE expanded in a localized basis in the laboratory frame  $F_o$

$$\begin{aligned}
i\hbar \frac{\partial}{\partial t_o} \left( \sum_{\alpha} C_{\alpha i}^o(t_o) \phi_{\alpha}^o(x_o) \right) \\
= \left[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x_o^2} + W_o(x_o) \right] \sum_{\alpha} C_{\alpha i}^o(t_o) \phi_{\alpha}^o(x_o).
\end{aligned} \tag{4.1.17}$$

This is exactly in the same form as that of equation (4.1.13). We can therefore see that corrections by the ETF on the basis functions and their coefficients allow us to work directly with the standard expression of TDSE and the standard Hamiltonian. However, the complexity of this approach comes when calculating the 4-center integrals of the Hamiltonian which have very complicated analytical forms and require huge computational effort. While this is achievable in small atomic systems made of two to three atoms [101] [102], the cost of computation will be enormous in our solid systems consisting of around a hundred atoms. In order to overcome this difficulty, we resolve to derive the TDSE without the ETF.

From this point on, we will stay in the laboratory frame and drop the index  $o$  for simplicity. To take into account of the implicit time dependence of GTO basis functions through the atom positions  $\mathbf{R}_A(t)$ , the partial time derivative has to be replaced by the total derivative [103]

$$\frac{\partial}{\partial t} \Rightarrow \frac{d}{dt} = \frac{\partial}{\partial t} + \sum_{A=1}^N \frac{\partial \mathbf{R}_A}{\partial t} \cdot \nabla_{\mathbf{R}_A} = \frac{\partial}{\partial t} + \sum_{A=1}^N \mathbf{v}_A \cdot \nabla_{\mathbf{R}_A}. \tag{4.1.18}$$

We define the product term of velocity and space gradient as operator  $\hat{D}$

$$\sum_{A=1}^N \mathbf{v}_A \cdot \nabla_{\mathbf{R}_A} = \hat{D}. \quad (4.1.19)$$

The left-hand side of (4.1.17) can now be derived as

$$\begin{aligned} i\hbar \frac{d}{dt} \left( \sum_{\alpha} C_{\alpha i}(t) \phi_{\alpha}(\mathbf{r} - \mathbf{R}_{A_{\alpha}}) \right) \\ = i\hbar \left[ \frac{\partial}{\partial t} + \hat{D} \right] \sum_{\alpha} C_{\alpha i}(t) \phi_{\alpha}(\mathbf{r} - \mathbf{R}_{A_{\alpha}}) \\ = i\hbar \sum_{\alpha} \left[ \frac{\partial}{\partial t} C_{\alpha i}(t) + C_{\alpha i}(t) \hat{D} \right] \phi_{\alpha}(\mathbf{r} - \mathbf{R}_{A_{\alpha}}). \end{aligned} \quad (4.1.20)$$

On the right-hand side of equation (4.1.17) the expression is not affected by the time-dependence of the basis functions. Hence we come down to an expression slightly different from the standard TDSE in equation (4.1.17)

$$i\hbar \sum_{\alpha} \left[ \frac{\partial}{\partial t} C_{\alpha i}(t) \right] \phi_{\alpha}(\mathbf{r} - \mathbf{R}_{A_{\alpha}}) = \left[ -\frac{\hbar^2}{2m} \nabla_{\mathbf{r}}^2 + W(\mathbf{r}) - i\hbar \hat{D} \right] \sum_{\alpha} C_{\alpha i}(t) \phi_{\alpha}(\mathbf{r} - \mathbf{R}_{A_{\alpha}}). \quad (4.1.21)$$

The addition of  $-i\hbar \hat{D}$  is exactly what bridges the gap between the frames  $F_v$  and  $F_o$ . Here we define the effective Hamiltonian operator whose similar expressions can also be found in references [103, 104]

$$\hat{M} = \hat{H} - i\hbar \hat{D}. \quad (4.1.22)$$

Projecting  $\langle \phi_{\beta}(\mathbf{r} - \mathbf{R}_{A_{\beta}}) |$  onto (4.1.21) gives us

$$i\hbar \sum_{\alpha} S_{\beta\alpha} \frac{\partial}{\partial t} C_{\alpha i}(t) = \left[ H_{\beta\alpha} - i\hbar D_{\beta\alpha} \right] \sum_{\alpha} C_{\alpha i}(t), \quad (4.1.23)$$

which can be reduced to the matrix form

$$i\hbar \frac{\partial}{\partial t} C = S^{-1} (H - i\hbar D) C. \quad (4.1.24)$$

This also gives us the effective Hamiltonian in the matrix form

$$M = S^{-1} (H - i\hbar D). \quad (4.1.25)$$

### 4.1.2 Properties and roles of $\hat{D}$

Now let us have a look at  $\hat{D}$  in its matrix form whose elements are expressed as

$$D_{\alpha\beta} = \left\langle \phi_{\alpha}(\mathbf{r} - \mathbf{R}_{A_{\alpha}}) \left| \mathbf{v}_{A'_{\beta}} \cdot \nabla_{\mathbf{R}_{A'_{\beta}}} \phi_{\beta}(\mathbf{r} - \mathbf{R}_{A'_{\beta}}) \right. \right\rangle. \quad (4.1.26)$$

Since we are in the laboratory frame, only the projectile ion has non-zero velocity  $\mathbf{v}_{proj}$ . This means that all elements in  $D$  that involves the target velocity are zero, thus giving  $D$  an asymmetric shape

$$D = \left( \begin{array}{cccc|cccc} & & & \vdots & & & & \vdots \\ & & & \vdots & & & & \vdots \\ \dots & \dots & 0 & \dots & \dots & \dots & \langle \phi_{target} | \mathbf{v}_{proj} \cdot \nabla_{\mathbf{R}_{proj}} \phi_{proj} \rangle & \dots \\ & & \vdots & & & & \vdots & \\ & & \vdots & & & & \vdots & \\ \hline & & \vdots & & & & \vdots & \\ \dots & \dots & 0 & \dots & \dots & \dots & \langle \phi_{proj} | \mathbf{v}_{proj} \cdot \nabla_{\mathbf{R}_{proj}} \phi_{proj} \rangle & \dots \\ & & \vdots & & & & \vdots & \end{array} \right). \quad (4.1.27)$$

This is a desired feature because in most cases the number of target basis functions is far greater than that of the projectile, which means more than half of the matrix elements do not require any calculations. The downside of this asymmetry is the loss of Hermitian property which can give  $D$  complex eigenvalues.

However, when the projectile is still as far from the target ions that there is no overlap between them, the block  $D_{target,proj} = \{ \langle \phi_{target} | \mathbf{v}_{proj} \cdot \nabla_{\mathbf{R}_{proj}} \phi_{proj} \rangle \}$  is zero. In addition the projectile-projectile block of  $D$  matrix is anti-Hermitian which we can prove from the fact that the overlap between two basis functions centered on the same atom does not alter in time

$$\frac{d}{dt} S_{AA} = \left\langle \frac{d}{dt} \phi_{\alpha}(\mathbf{r} - \mathbf{R}_{A_{\alpha}}) \left| \phi_{\beta}(\mathbf{r} - \mathbf{R}_{A'_{\beta}}) \right. \right\rangle + \left\langle \phi_{\alpha}(\mathbf{r} - \mathbf{R}_{A_{\alpha}}) \left| \frac{d}{dt} \phi_{\beta}(\mathbf{r} - \mathbf{R}_{A'_{\beta}}) \right. \right\rangle = 0. \quad (4.1.28)$$

The transpose-conjugate of an element in the block  $D_{proj,proj}$  reads

$$\left\langle \phi_{\alpha}(\mathbf{r} - \mathbf{R}_{proj}) \left| \frac{d}{dt} \phi_{\beta}(\mathbf{r} - \mathbf{R}_{proj}) \right. \right\rangle^H = \left\langle \frac{d}{dt} \phi_{\beta}(\mathbf{r} - \mathbf{R}_{proj}) \left| \phi_{\alpha}(\mathbf{r} - \mathbf{R}_{proj}) \right. \right\rangle. \quad (4.1.29)$$

Combining with the relation (4.1.28) we show that

$$\left\langle \phi_\alpha(\mathbf{r} - \mathbf{R}_{proj}) \left| \frac{d}{dt} \phi_\beta(\mathbf{r} - \mathbf{R}_{proj}) \right. \right\rangle^H = - \left\langle \phi_\beta(\mathbf{r} - \mathbf{R}_{proj}) \left| \frac{d}{dt} \phi_\alpha(\mathbf{r} - \mathbf{R}_{proj}) \right. \right\rangle, \quad (4.1.30)$$

thus

$$D_{proj,proj}^H = -D_{proj,proj}. \quad (4.1.31)$$

It is worth pointing out that the total overlap matrix  $S$  still varies in time due to the crossed terms where the two basis functions are centered on different atoms, and in a general form we can write

$$\frac{d}{dt}S = D^H + D. \quad (4.1.32)$$

Since only the projectile-projectile block is non-zero at the beginning of the propagation, the  $D$  matrix is anti-Hermitian, making the effective Hamiltonian  $M$  a Hermitian matrix. The diagonalization of the Hermitian  $M$  produces real eigenvalues and stable eigenstates. When the projectile is well separated from the target before their collision, the electron density of the system is not yet perturbed. Since there is almost no overlap between the two entities, the Hamiltonian  $H$  and the effective Hamiltonian  $M$  are both constant in time. This results in constant total energy of the system.

After the collision, when there is no basis on the projectile, the total energy of the Hamiltonian  $H$  will again become constant as the two entities part away from each other and their interactions fade. The situation is different with the projectile basis present since electrons are allowed to bond with the projectile and waves of electron density will continue to oscillate around the projectile. As a consequence, the total energy of the Hamiltonian  $H$  keeps oscillating after the collision. However, this extra dynamics is compensated by the energy contribution from  $-i\hbar D$  and the total energy of the effective Hamiltonian  $M$  will eventually go back to a constant value as  $M$  regains its Hermitian status. The energy represented by  $-i\hbar D$  will be further discussed later in this section and the detailed example of the energy compensation will be given in diatomic systems in Chapter 4.

Another important role of  $D$  is to conserve the orthonormality of wave functions:

$$\frac{d}{dt}C^H S C = 0. \quad (4.1.33)$$

Let us now develop equation (4.1.33) with the help of relation (4.1.32) and replace all time

derivatives of coefficient matrix  $C$  by expression (4.1.24). Keep in mind that matrices  $H$  and  $S$  are both Hermitian thus invariant to the conjugate transpose operation.

$$\begin{aligned}
\frac{d}{dt}C^H SC &= \left(\frac{\partial}{\partial t}C^H\right)SC + C^H\left(\frac{d}{dt}S\right)C + C^H S\left(\frac{\partial}{\partial t}C\right) \\
&= C^H\left(\frac{i}{\hbar}H - D^H\right)S^{-1}SC + C^H(D^H + D)C \\
&\quad + C^H S\left[-S^{-1}\left(\frac{i}{\hbar}H - D\right)\right]C \\
&= C^H\left(\frac{i}{\hbar}H - D^H\right)C + C^H(D^H + D)C - C^H\left(\frac{i}{\hbar}H - D\right)C \\
&= 0.
\end{aligned} \tag{4.1.34}$$

Hereby we have proven the orthonormality of wave functions to be conserved during the entire propagation. This would not be the case if we use the simple Hamiltonian  $H$  instead of  $(H - i\hbar D)$  due to the time dependency of the overlap matrix  $S$ .

One more thing worth discussing here is the homogeneity of  $-i\hbar\hat{D}$  to an energy that we can obtain from the trace of matrix product between the density matrix  $P$  and  $D$

$$\begin{aligned}
E_{-iD} &= -i\hbar\text{Tr}\{PD\} \\
&= -i\hbar\sum_{\alpha\beta}P_{\alpha\beta}D_{\alpha\beta} \\
&= -i\hbar\sum_i\sum_{\alpha\beta}f_iC_{\beta i}C_{\alpha i}^*\langle\phi_\alpha|\mathbf{v}_{A'_\beta}\cdot\nabla_{\mathbf{R}_{A'_\beta}}\phi_\beta\rangle.
\end{aligned} \tag{4.1.35}$$

Here  $f_i$  is the occupation number for the electronic state  $i$  that can be either 1 (occupied) or 0 (unoccupied). Let us recall the momentum operator to be

$$\hat{\mathbf{p}} = -i\hbar\nabla_{\mathbf{r}}. \tag{4.1.36}$$

A relation exists between the two gradients [103]

$$\begin{aligned}
\nabla_{\mathbf{r}}\phi_\alpha(\mathbf{r} - \mathbf{R}_{A_\alpha}) &= -\nabla_{\mathbf{R}_{A_\alpha}}\phi_\alpha(\mathbf{r} - \mathbf{R}_{A_\alpha}) \\
&\equiv -\sum_{A=1}^N\nabla_{\mathbf{R}_A}\phi_\alpha(\mathbf{r} - \mathbf{R}_{A_\alpha}).
\end{aligned} \tag{4.1.37}$$

The expectation value of  $\hat{\mathbf{p}}$  acting on the one-particle functions can be expressed as

$$\begin{aligned}
\langle \psi_i(\mathbf{r}, t) | \hat{\mathbf{p}} | \psi_i(\mathbf{r}, t) \rangle &= \int d\mathbf{r}^3 \sum_{\alpha\beta} C_{\alpha i}^*(t) \phi_\alpha(\mathbf{r} - \mathbf{R}_{A_\alpha}) (-i\hbar \nabla_{\mathbf{r}}) C_{\beta i}(t) \phi_\beta(\mathbf{r} - \mathbf{R}_{A'_\beta}) \\
&= i\hbar \sum_{\alpha\beta} C_{\alpha i}^*(t) C_{\beta i}(t) \int d\mathbf{r}^3 \phi_\alpha(\mathbf{r} - \mathbf{R}_{A_\alpha}) \nabla_{\mathbf{R}_{A'_\beta}} \phi_\beta(\mathbf{r} - \mathbf{R}_{A'_\beta}) \quad (4.1.38) \\
&= i\hbar \sum_{\alpha\beta} C_{\alpha i}^*(t) C_{\beta i}(t) \langle \phi_\alpha | \nabla_{\mathbf{R}_{A'_\beta}} \phi_\beta \rangle.
\end{aligned}$$

This gives another way to define  $E_{-iD}$

$$E_{-iD} = - \sum_i f_i \langle \psi_i | \mathbf{v} \cdot \hat{\mathbf{p}} | \psi_i \rangle \quad (4.1.39)$$

We now prove that the expectation value in (4.1.38) can also be obtained from writing

$$\langle \hat{\mathbf{p}} \rangle = m \frac{d\langle \hat{x} \rangle}{dt}. \quad (4.1.40)$$

This relation is obtained thanks to Ehrenfest's theorem [105] on the time derivation of expectation values of quantum operators

$$\begin{aligned}
\frac{d}{dt} \langle \hat{A} \rangle &\equiv \frac{d}{dt} \langle \Psi | \hat{A} | \Psi \rangle = \left\langle \frac{d\Psi}{dt} | \hat{A} | \Psi \right\rangle + \langle \Psi | \frac{d\hat{A}}{dt} | \Psi \rangle + \left\langle \Psi | \hat{A} | \frac{d\Psi}{dt} \right\rangle \\
&= -\frac{1}{i\hbar} \langle \hat{H} \Psi | \hat{A} | \Psi \rangle + \frac{1}{i\hbar} \langle \Psi | \hat{A} | \hat{H} \Psi \rangle + \langle \Psi | \frac{d\hat{A}}{dt} | \Psi \rangle \\
&= \frac{1}{i\hbar} \langle \Psi | [\hat{A}, \hat{H}] | \Psi \rangle + \langle \Psi | \frac{d\hat{A}}{dt} | \Psi \rangle \\
&\equiv \frac{1}{i\hbar} \langle [\hat{A}, \hat{H}] \rangle + \left\langle \frac{d\hat{A}}{dt} \right\rangle. \quad (4.1.41)
\end{aligned}$$

If we put the position operator  $\hat{x}$  at the place of  $\hat{A}$  we get

$$\begin{aligned}
\frac{d}{dt} \langle \hat{x} \rangle &= \frac{1}{i\hbar} \langle [\hat{x}, \hat{H}] \rangle + \left\langle \frac{d\hat{x}}{dt} \right\rangle \\
&= \frac{1}{i\hbar} \left\langle \left[ \hat{x}, \frac{\hat{\mathbf{p}}^2}{2m} + \hat{V} \right] \right\rangle \\
&= \frac{1}{2im\hbar} \langle [\hat{x}, \hat{\mathbf{p}}] \hat{\mathbf{p}} + \hat{\mathbf{p}} [\hat{x}, \hat{\mathbf{p}}] \rangle \\
&= \frac{1}{2im\hbar} (i\hbar \langle \hat{\mathbf{p}} \rangle + \langle \hat{\mathbf{p}} \rangle i\hbar) \\
&= \frac{\langle \hat{\mathbf{p}} \rangle}{m}. \quad (4.1.42)
\end{aligned}$$

This gives us exactly equation (4.1.40). Let us now integrate both sides in time

$$\begin{aligned} \int_{t_0}^t \langle \hat{\mathbf{p}} \rangle dt &= m \int_{t_0}^t \frac{d\langle \hat{x} \rangle}{dt} dt, \\ (t - t_0) \langle \hat{\mathbf{p}} \rangle &= m (\langle \hat{x} \rangle_t - \langle \hat{x} \rangle_{t_0}). \end{aligned} \quad (4.1.43)$$

For a system whose particles all move together at a constant velocity, we can further write

$$\langle \hat{\mathbf{p}} \rangle = m \frac{\langle \hat{x} \rangle_t - \langle \hat{x} \rangle_{t_0}}{t - t_0} = m \mathbf{v}. \quad (4.1.44)$$

Here we introduce the Mulliken charge  $q_i$  in electronic state  $i$  which can be a fractional number in numerical simulations

$$q_i = \sum_{\alpha\beta} \langle \psi_i | \phi_\alpha \rangle S_{\alpha\beta}^{-1} \langle \phi_\beta | \psi_i \rangle. \quad (4.1.45)$$

At last, when we plug (4.1.44) and (4.1.45) back into (4.1.39) we have

$$E_{-iD} = -m\mathbf{v}^2 \sum_i f_i q_i = -m_q \mathbf{v}^2, \quad (4.1.46)$$

where  $m_q$  represents the mass of all moving electrons. This demonstrates that the representative energy of the term  $-i\hbar\hat{D}$  takes up twice the amount of kinetic energy of the moving electrons. While we have not reached an analytical expression to prove the relation (4.1.46) for systems with only one moving particle, numerical studies has confirmed this relation as we shall see in the next section.

### 4.1.3 Numerical study of $\hat{D}$

In the previous discussion we have explained how the operator  $\hat{D}$  in equation (4.1.19) ensures the Gallilean invariance when transforming the ground-state wave functions obtained in the projectile's frame into the laboratory frame. Numerically this is achieved by finding the Self-Consistent Field (SCF) solutions of the stationary Kohn-Sham equation using the effective Hamiltonian  $\hat{M}$  in expression (4.1.22) instead of the standard  $\hat{H}$ . This step involves iterative cycles of calculations to reach convergence and can be considered as the re-initialization of the ground-state wave functions  $\Psi_o$ .

Ideally at convergence, if we had a complete basis set, the eigen energy  $E_v$  of the effective

Hamiltonian with the updated wave functions  $\Psi_v$  would be lower than  $E_o$  of the original Hamiltonian with the original  $\Psi_o$  by exactly one unit of the electron kinetic energy. The mathematical explanation for this energy shift can be established from equation (4.1.16) which we simplify as

$$\hat{H}e^{-if}\Psi_o = e^{-if}\hat{H}\Psi_o + \frac{m\mathbf{v}^2}{2}e^{-if}\Psi_o + e^{-if}i\hbar\mathbf{v} \cdot \nabla_{\mathbf{r}}\Psi_o. \quad (4.1.47)$$

Using relations (4.1.3) and (4.1.37) we then get

$$\hat{H}\Psi_v = e^{-if}\hat{H}\Psi_o + \frac{m\mathbf{v}^2}{2}\Psi_v - e^{-if}i\hbar\hat{D}\Psi_o. \quad (4.1.48)$$

The stationary Schrödinger equation in the laboratory frame being

$$\hat{H}\Psi_o = E_o\Psi_o, \quad (4.1.49)$$

allowing us to replace the first term in equation (4.1.48)

$$\hat{H}\Psi_v = E_o\Psi_v + \frac{m\mathbf{v}^2}{2}\Psi_v - e^{-if}i\hbar\hat{D}\Psi_o. \quad (4.1.50)$$

Now we aim to rewrite the last term in equation (4.1.50) without the factor  $e^{-if}$  starting from

$$i\hbar\hat{D}\Psi_v = i\hbar\mathbf{v} \cdot \nabla_{\mathbf{R}}\Psi_v \quad (4.1.51)$$

Introducing relation (4.1.3) and deriving the above equation gives us:

$$i\hbar\hat{D}\Psi_v = m\mathbf{v}^2\Psi_v - e^{-if}i\hbar\hat{D}\Psi_o. \quad (4.1.52)$$

Inserting (4.1.52) back to (4.1.50) leads to:

$$\hat{H}\Psi_v = E_o\Psi_v + \frac{m\mathbf{v}^2}{2}\Psi_v + i\hbar\hat{D}\Psi_v - m\mathbf{v}^2\Psi_v, \quad (4.1.53)$$

which after some reordering becomes

$$(\hat{H} - i\hbar\hat{D})\Psi_v = (E_o - \frac{m\mathbf{v}^2}{2})\Psi_v. \quad (4.1.54)$$

Projecting the above equation onto  $\Psi_v$  eventually makes

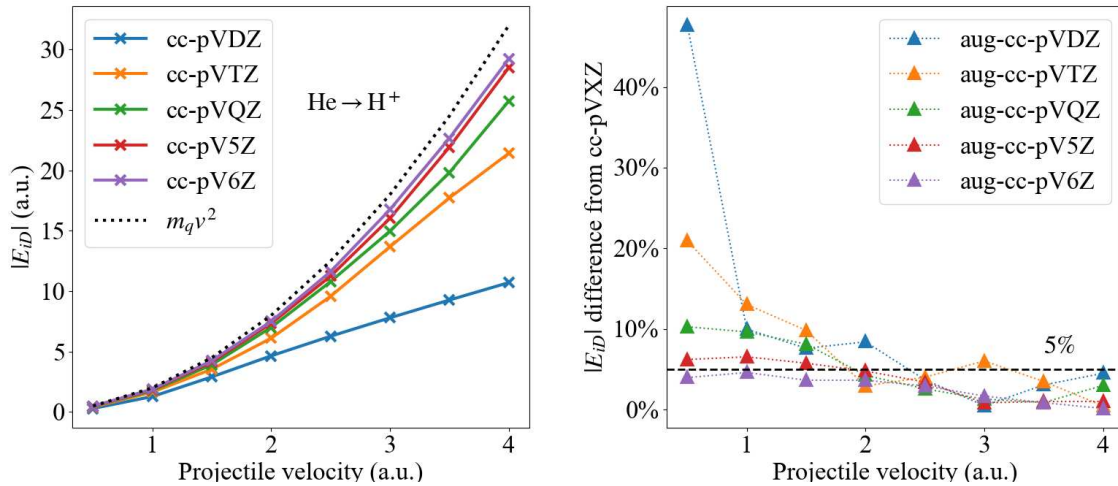
$$E_v = E_o - \frac{m_q \mathbf{v}^2}{2} = E_o + \frac{1}{2} E_{-iD}, \quad (4.1.55)$$

where  $E_{-iD}$  comes from equation (4.1.46).

However, since basis completeness is not achievable in the real world, we can only obtain an approximation of the relation (4.1.3) using the converged eigenstates of the effective Hamiltonian

$$\Psi_{H-ihD} \approx \Psi_v = e^{-if} \Psi_o. \quad (4.1.56)$$

The accuracy of relation (4.1.55), which comes down to the accuracy of  $E_{-iD}$ , depends therefore largely on the quality of the ETF approximation in equation (4.1.56) which is tightly bound to the basis set quality and has larger error at higher projectile velocity.



**Figure 4.1.1:** Energy approximation of  $m_q v^2$  with  $E_{-iD}$  for a helium projectile traveling towards a proton (same basis as helium). The left-side image traces the absolute value of  $E_{-iD}$  for the standard basis sets cc-pVXZ. The black dotted curve represents the theoretical value of projectile charge kinetic energy  $m_q v^2$ . The curves in solid lines each represents a basis quality with a different color ranging from the lowest cardinal number  $X = D$  to the highest  $X = 6$ . The right-side image compares the accuracy in percentage between the standard basis and the augmented basis aug-cc-pVXZ at different velocities. Both basis sets share the same color assignment.

Figure 4.1.1 demonstrates to which degree basis quality and projectile velocity influence the estimation of  $E_{-iD}$  for a diatomic system with helium projectile (possessing two electrons) and proton target. On the left side the image shows the deviation of  $|E_{-iD}|$  from the theoretical value  $m_q v^2$  as the projectile velocity rises and the basis quality goes from low (DZ) to high (6Z).  $v$  is reduced to one dimension for simplicity. On the right side,

comparison between the standard basis cc-pVXZ and the augmented basis aug-cc-pVXZ is realized. Tolerating a 5% deviation, we notice that the improvement on  $|E_{-iD}|$  brought from the augmented basis becomes more important at lower velocity and for smaller cardinal number  $X$ . This means that we can use a high quality standard basis, cc-pV6Z for example, instead of an augmented basis to economize on the simulation costs and still get good energy precision.

Coming back to the SCF cycles, although it provides a fast way to reinitialize the wave functions, it is only practical for atomic systems with a small number of atoms. For solid systems like metals, the SCF convergence with the effective Hamiltonian is too difficult to reach. We have attempted to help the convergence by applying energy corrections based on the shifting of projectile-occupied energy levels as a consequence of electrons moving with the projectile. With the most complete basis set available and at a large target-projectile distance we expect a shifted value of  $v^2/2$  in atomic units where  $v$  stands for the projectile velocity. For causes yet unknown, this does not agree with the numerical observations which reports very little shifting. On the other hand if we position the projectile close to or within the target we do observe the energy level shifting. At the same time the hybridization of orbitals often take place and make it impossible to isolate states occupied solely by the projectile for energy corrections. As an alternative solution, we consider it more convenient in these cases to let the system start directly from the ground-state and find its new equilibrium after some transition period.

## 4.2 Modifications in Propagators

Presented in Chapter 2, the second-order Magnus (MAG2) propagator and the Crank-Nicolson (CN) propagator are the two main propagators used in MOLGW. Although the MAG2 is shown to be more reliable than the CN for situations without projectile basis, it is no longer the best option when projectile basis is applied. In the following discussions we will explain the choice of propagator regarding the presence of projectile basis.

**Second-order Magnus propagator.** When simulating with projectile basis, the operator matrix  $M$  in equation (2.3.27) cannot stay Hermitian due to the presence of  $D$  (explained in section 4.1.2) and loses the quality to be diagonalized on the orthogonal basis. The propagator  $\hat{U}_{MAG2}$  is therefore no longer unitary. Moreover, to avoid diagonalizing  $M$

in the non-orthogonal basis we can use a truncated Taylor expansion of the exponential term in (2.3.27)

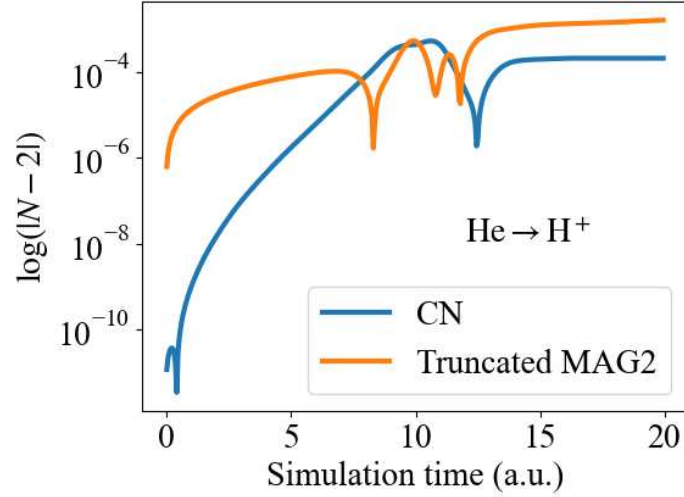
$$\hat{U}_{MAG2}(t + \Delta t, t) \approx \hat{I} - i\Delta t \hat{M}(t + \frac{\Delta t}{2}) - \frac{1}{2}(\Delta t)^2 \hat{M}^2(t + \frac{\Delta t}{2}). \quad (4.2.1)$$

Although we can mitigate the violation of unitarity by using tiny time steps and including more expanded terms in (4.2.1) to increase precision, it is obvious that the truncated version of  $\hat{U}_{MAG2}$  is far less exact than its original form. We have thus lost all benefits from this propagator as established for systems without projectile basis.

**Crank-Nicolson propagator.** Like MAG2, the CN propagator faces the same problem of losing unitarity with the non Hermitian matrix  $M$ . However, compared to a truncated MAG2 in equation (4.2.1), no compromises are needed for using the CN propagator in this basis setting. This means that the CN propagator might have stabler performances than the truncated MAG2 propagator. One way to validate this hypothesis is to verify the orthonormality conservation of the wave functions  $\psi_i(t)$  as stated in equation (4.1.33), which can be reflected as the conservation of total electron number  $N$

$$\frac{d}{dt} \sum_i \langle \psi_i(t) | \psi_i(t) \rangle = \frac{dN}{dt} = 0. \quad (4.2.2)$$

Figure 4.2.1 shows the errors in total electron conservation for both the CN and the second-order truncated MAG2 propagator in a diatomic system of helium projectile and proton target. Although tiny in magnitude, we can still see that the truncated MAG2 propagator generates more error than the CN propagator throughout the entire simulation, even for such a simple system. While it is possible to improve the truncated MAG2 by including higher orders in expression (4.2.1), it also adds more matrix multiplications of  $M$  which will make the code slower than using the CN propagator. This is already the case for the second-order MAG2 propagator which requires one matrix inversion of dimension  $N_{BF} \times N_{BF}$  and three matrix multiplications of dimension  $N_{BF} \times N_{BF}$ , which counts one multiplication more than for the CN propagator. Hereby considering both the accuracy and the efficiency, we prefer  $\hat{U}_{CN}$  for systems with projectile basis.



**Figure 4.2.1:** Electron conservation errors with CN and truncated MAG2 propagators for a system of He projectile (TZ) and proton target (TZ). The time step used is 0.05 a.u. (1.2 as) and the errors are reported in log-scale of the difference between estimated electron number  $N$  and the theoretical number of two electrons. Errors from the CN propagator is traced with the blue line, and errors from the truncated MAG2 propagator is traced with the orange line. The x-axis denotes the simulation time in atomic units.

To sum up this chapter, we have discussed about the need to change reference frames when doing real-time simulations of ion irradiation. As we add basis functions to the projectile, the time-dependent equations gains a new operator  $\hat{D}$  with specific properties. In consequence, the propagators are modified and their reliability re-evaluated. In the next chapter we will present some important aspects of numerical implementation and several tests used to validate our code.

## Chapter 5

# Numerical Development and Validation of Code

Detailed numerical development for the real-time TDDFT propagation will be presented in this chapter as well as some optimization techniques. We then demonstrate the energy treatment for simulations with atomic targets and validate our code with several functionality tests in atomic systems.

## 5.1 Implementation and Optimisation

There are two main objectives for the implementation. We first need to make sure that the center of projectile basis updates its position correctly as the projectile center moves. Then we have to take into account of the projectile basis movement by implementing the operator  $\hat{D}$  into the propagation process. The real-time updates of the projectile basis require recalculations of multiple integrals and matrices and will in consequence increase simulation costs. One key optimization is to reduce the number of items to be recalculated. At the same time we should minimize the number of repetitions.

### 5.1.1 Tracking projectile basis

In order to differentiate from existing modules that execute without the projectile basis, a new scenario is defined in the code to execute options designed for projectiles with basis. The first thing to do is to update the center of projectile basis whenever the projectile

moves. Then we need to feed that piece of information to all basis functions localized on the projectile. Inside MOLGW, a basis set is programmed as an object class with several attributes including the electron shells and the basis functions. These two attributes mentioned are themselves defined as object classes with their own attributes such as the index of corresponding atoms and the basis center positions. This is where we update the basis function movement. It is also useful to add the velocity of moving centers as a new attribute. Among all atoms in the system, only the projectile has non-zero velocity. We can thus use this information to correctly identify projectile basis functions rather than looking at the atom index. The same update process applies for the auxiliary basis. Furthermore, since the target atoms do not require positional updates, we can split the basis into a target part and a projectile part to optimize the updates. More discussions on this will be brought up in the later section of partial matrix calculations.

Another crucial feature to implement is the analytical calculation of the gradient matrix  $D$ . Observing its expression in equation (4.1.26) we can rewrite

$$\begin{aligned} D_{\alpha\beta} &= \left\langle \phi_\alpha(\mathbf{r} - \mathbf{R}_{A_\alpha}) \left| \nabla_{\mathbf{R}_{A'_\beta}} \phi_\beta(\mathbf{r} - \mathbf{R}_{A'_\beta}) \right. \right\rangle \cdot \mathbf{v}_{A'_\beta} \\ &= \left\langle \nabla_{\mathbf{R}_{A'_\beta}} \phi_\beta(\mathbf{r} - \mathbf{R}_{A'_\beta}) \left| \phi_\alpha(\mathbf{r} - \mathbf{R}_{A_\alpha}) \right. \right\rangle^H \cdot \mathbf{v}_{A'_\beta} = \mathbf{L}_{\beta\alpha}^H \cdot \mathbf{v}_{A'_\beta}. \end{aligned} \quad (5.1.1)$$

Here we define matrix  $\mathbf{L}$  as the left gradient of the overlap matrix  $S$

$$\mathbf{L}_{\alpha\beta} = \left\langle \nabla_{\mathbf{R}_{A_\alpha}} \phi_\alpha(\mathbf{r} - \mathbf{R}_{A_\alpha}) \left| \phi_\beta(\mathbf{r} - \mathbf{R}_{A'_\beta}) \right. \right\rangle. \quad (5.1.2)$$

In matrix form equation (5.1.1) becomes

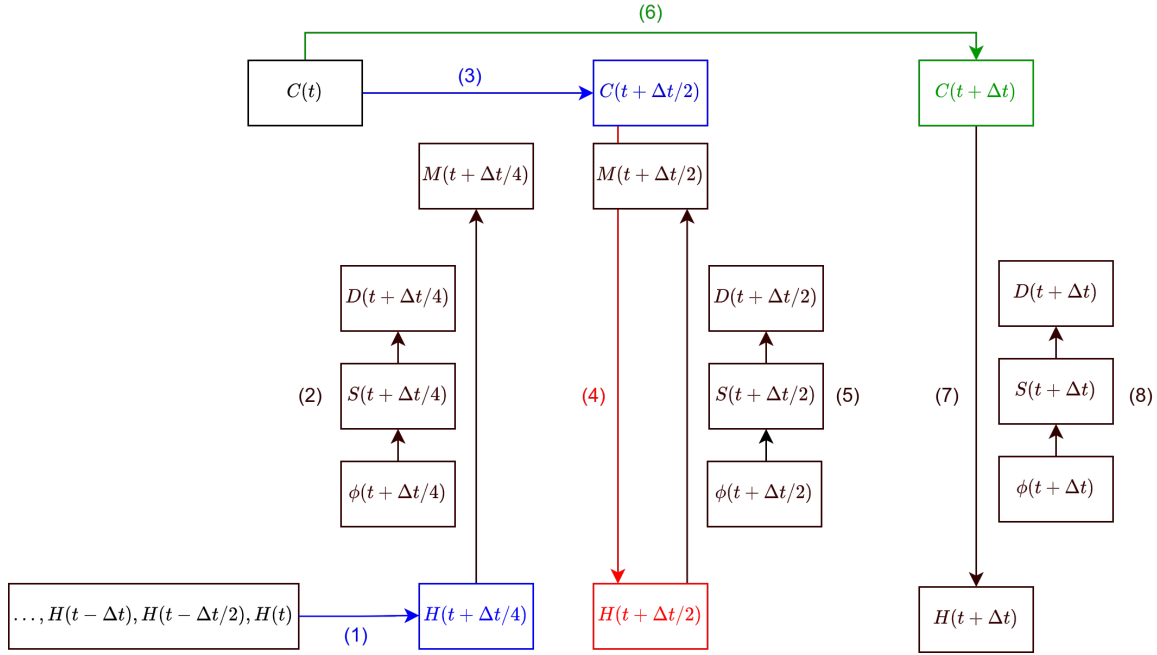
$$D = \mathbf{L}^H \cdot \mathbf{v}_{basis}, \quad (5.1.3)$$

where  $\mathbf{v}_{basis}$  denotes the velocity matrix of basis centers with dimension  $3 \times N_{BF}$  and matrix  $\mathbf{L}$  has the dimension  $N_{BF} \times N_{BF} \times 3$ . The numerical calculation of  $D$  matrix is thus straightforward as we first evaluate matrix  $\mathbf{L}$ , then take its transpose-conjugate and multiple by the velocity matrix  $\mathbf{v}_{basis}$ . Being a time-dependent term, matrix  $D$  requires updates at each time step. As we will see later, this recalculation process can be optimized.

## 5.1.2 Predictor-corrector scheme

In chapter 2 we have talked about how to use the CN propagator (2.3.33) to evolve wave functions from instant  $t$  to  $t + \Delta t$ . We have also seen in expression (2.3.26) that the propagation of wave functions can be realized by propagating the coefficient matrix  $C(t)$ . To construct the CN propagator, we need to evaluate the operator  $M$  in equation (4.1.22) at the mid-point  $t + \frac{\Delta t}{2}$ . The overlap matrix  $S$  and the gradient matrix  $D$  can both be calculated analytically. The remaining term  $H(t + \frac{\Delta t}{2})$  can be obtained through the extrapolation of previous Hamiltonian matrices, but a more accurate estimation requires a finer strategy [76]. Adapting the Predictor-Corrector (PC) scheme from Cheng [106] to our CN propagator we build the following steps:

- (1) (Predictor) Extrapolate  $H(t + \frac{\Delta t}{4})$  from a record of  $H(\tau \leq t)$  evaluated at every  $\frac{\Delta t}{2}$  step.
- (2) Update the basis centers then calculate  $S(t + \frac{\Delta t}{4})$  and  $D(t + \frac{\Delta t}{4})$  to get  $M(t + \frac{\Delta t}{4})$ .
- (3) (Predictor) Propagate  $C(t) \rightarrow C(t + \frac{\Delta t}{2})$  using  $M(t + \frac{\Delta t}{4})$  in the CN propagator.
- (4) (Corrector) Update the basis and auxiliary basis centers then evaluate  $H(t + \frac{\Delta t}{2})$  using  $C(t + \frac{\Delta t}{2})$ .
- (5) Update  $S$  and  $D$  to  $t + \frac{\Delta t}{2}$  and evaluate  $M(t + \frac{\Delta t}{2})$ .
- (6) (Propagation) Propagate  $C(t) \rightarrow C(t + \Delta t)$  with  $M(t + \frac{\Delta t}{2})$ .
- (7) Update the basis and auxiliary basis centers then evaluate  $H(t + \Delta t)$  with  $C(t + \Delta t)$ .
- (8) Update  $S$  and  $D$  to instant  $t + \Delta t$ .



**Figure 5.1.1:** Predictor-corrector scheme with the CN propagator. The diagram is composed of eight numerated steps to describe the propagation of coefficient matrix  $C$  from instant  $t$  to  $t + \Delta t$ . Paths colored in blue represent the predictor steps (1) and (3) and the corrector step (4) is represented by the red color. The propagation step (6) is colored in green while the update steps (2), (5), (7) and (8) are colored in black.

The diagram in Figure 5.1.1 helps to illustrate these steps of propagation. We can divide the scheme into different parts. Steps (1) and (3) are the predictors since the Hamiltonian  $H(t + \Delta t/4)$  comes from extrapolation instead of *ab initio* evaluation. Step (4) is the corrector that gives an evaluated  $H(t + \Delta t/2)$  from the coefficient matrix  $C(t + \Delta t/2)$ . Step (6) propagates the system from  $t$  to  $t + \Delta t$  using the effective Hamiltonian  $M(t + \Delta t/2)$  at midpoint. The rest of the steps (2), (5), (7) and (8) updates the system to the correct time-point.

Using a predictor-corrector scheme such as described above not only gives better accuracy than the simple extrapolation of the the midpoint Hamiltonian  $H(t + \Delta t/2)$ , it also saves us from evaluating  $H(t + \Delta t/2)$  in a more costly iterative manner [76, 106]. We also carefully keep the time step  $\Delta t$  under 0.05 a.u. (1.2 as) to ensure better precision.

### 5.1.3 Partial calculations of matrices

We can see from the above PC scheme that there are a lot of matrix updates happening at each propagation time step. Apart from  $S$  and  $D$ , all terms inside  $H$  in equation (2.2.13) need to be recalculated. The dimension of basis-related matrices such as  $S$ ,  $D$ ,  $T$  and  $V$

is  $N_{BF} \times N_{BF}$ , while the calculations of  $V_H$  involves auxiliary-basis-related 2-center and 3-center integral matrices of the size  $N_{ABF} \times N_{ABF}$  and  $N_{BF}^2 \times N_{ABF}$ . Remember that we have mentioned in Chapter 2, both  $N_{BF}$  and  $N_{ABF}$  can get to the order of thousands in solid systems, making it a laborious task to recalculate the entire matrices.

Actually it is unnecessary to do the full recalculations. Let us take matrix  $S$  for example

$$S = \left( \begin{array}{ccc|ccc} & & & & & \\ & & & & & \\ & & & & & \\ \vdots & & & & & \\ \dots & S_{TT} & \dots & S_{TP} & & \\ & & & & & \\ & & & & & \\ \vdots & & & & & \\ \hline & & & & & \\ \dots & S_{PT} & \dots & S_{PP} & & \end{array} \right) \quad (5.1.4)$$

Here we have divided the matrix into four sub-matrices according to the coupling between basis centers. The notation  $T$  signifies the target basis functions and  $P$  the projectile basis functions. Since the center positions stay relatively fixed between two target functions or two projectile functions, we can skip the recalculations of  $S_{TT}$  and  $S_{PP}$ , leaving us only the crossover terms to reevaluate. In general the target functions outnumber the projectile functions as there is only one projectile in the system. This means that we are saving at least and usually far more than half of the computation by partially recalculating the matrices. In the case of proton impinging aluminum, we could have only 5 basis functions on the proton using the cc-pVDZ basis while 4400 on aluminum atoms using the cc-pCVQZ basis. The extreme skewness of the resulting matrices allows us to save up to 99% of the recalculations on  $S$ ,  $D$ ,  $T$  and  $V$  in solid targets which translates to up to 10 human hours spared for a single-trajectory calculation. The same techniques are used on the 2-center and 3-center integral matrices during the evaluation of the Hartree term  $V_H$  in equation (2.2.19).

Similar to the 2-center integrals, we can divide the 3-center integral matrices by blocks of target (T) and projectile (P) basis combination and skip the homogeneous products like  $(\alpha_T \beta_T | K_T)$  and  $(\alpha_P \beta_P | K_P)$ . However, doing so still leave us with a large number of elements to be recalculated. It turns out that we can further optimize this process by improving the integral screening. Since two basis functions can have very small overlap when their basis centers are far from each other, their contributions to the energy are nearly negligible and the pair can be screened out before the integral calculations. The tolerance for the minimum overlap can be adjusted flexibly in MOLGW. The smaller the tolerance,

the less pairs are screened out and the higher the integral evaluation quality would be. This screening is carried out only once and ahead of any Hamiltonian evaluations. As the projectile moves, the overlap between projectile and target basis function would change at each time step. It is thus more convenient to keep all mixed pairs between target and projectile for recalculations. However, the screening is useful on the target-target block and reduces significantly the memory allocation in large solid systems. As we use elongated solid target in this work, the economy on CPU memory can reach 50% for an aluminum cluster of 3.2 Å in radius and 24 Å in length.

We would like to point out that for the exchange-correlation term  $V_{xc}$  the calculations are realized on a discretized grid which has to be updated at each time step with the basis center displacement. There is currently no optimization done concerning its reevaluation since it only takes a small portion of the total calculation time. Nonetheless it counts as part of the potential improvements of the MOLGW code.

## 5.2 Functionality Test

Once all implementations are in place we seek to test our code. These tests need to be quick to run, give qualitative insights and satisfy key conditions. Simple diatomic systems are therefore the ideal candidates for these purposes. In this section we will first explain the energy treatments needed for atomic systems before presenting three important validation tests.

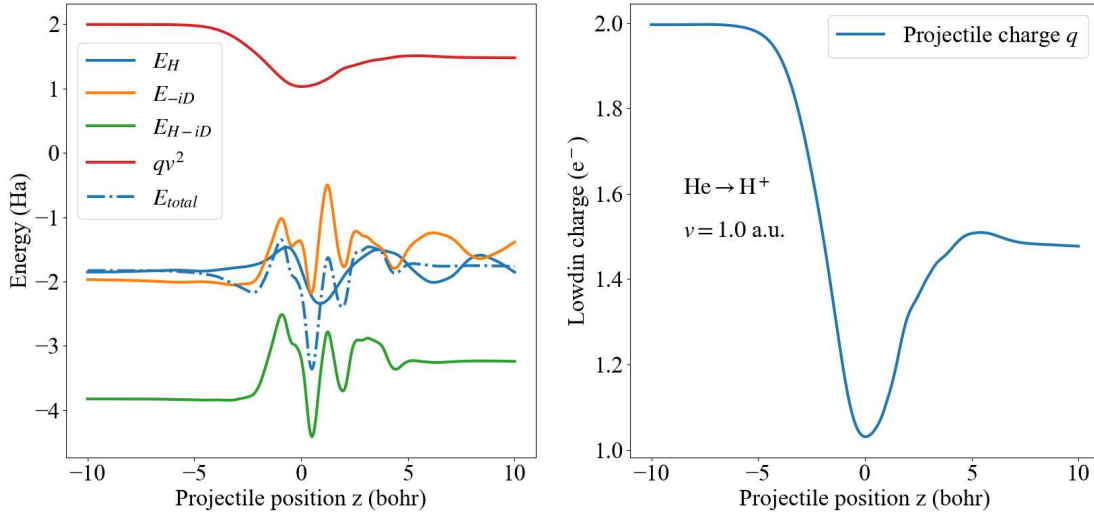
### 5.2.1 Energy treatments in atomic systems

We have previously seen in figure 2.4.1 how the energy varies when a projectile travels through a solid target. This profile would look slightly different in a diatomic system since the encounter only happens once. Figure 5.2.1 gives a clear explanation of how the energy is treated when a helium atom travels by a proton at  $v = 1.0$  a.u. (100 keV). A6Z basis set is applied to both particles in order to demonstrate results with the best precision, as well as in all other diatomic systems in this section. The target is placed at the origin of the z-axis along which the projectile travels. We have already discussed in section 3.2.2 that the energy of the standard Hamiltonian  $H$  (represented by the blue solid line) after the collision is unstable due to the oscillation of the electronic charge around the projectile

center. However, thanks to the compensation of  $E_{-iD}$  (in orange line) the energy of the effective Hamiltonian  $M = H - iD$  (in green line) returns to a constant value. We have also established in equation (4.1.46) that  $E_{-iD}$  equals to twice of the kinetic contribution of the projectile charge  $q$  (in red line). Here we consider the Löwdin charge which is calculated as [73]

$$q = \text{Tr}\{S^{1/2}PS^{1/2}\}. \quad (5.2.1)$$

By adding  $qv^2$  back to  $E_{H-iD}$ , we raise the total energy (in blue broken line with dots) back to the same level as  $E_H$ . The evolution of the projectile charge  $q$  is given at the right side of the figure, and is constant 7 bohr ( $3.7 \text{ \AA}$ ) away from the target center. About 0.5 electron is lost after the projectile-target impact. The fractional electron number does not make any physical sense, but it gives a qualitative insight on the charge exchange between the two particles.



**Figure 5.2.1:** Energy treatment of helium hitting proton at  $v = 1.0 \text{ a.u.}$  (100 keV). The proton target is placed at  $z = 0$  bohr on the projectile trajectory along the  $z$ -axis. On the left panel we show the energy profile of the system. The energy of Hamiltonian  $E_H$  is traced with a blue solid line. The energy contribution of  $-iD$  is traced with an orange line. The green line represents the energy of the effective Hamiltonian  $E_{H-iD}$  and the red line represents twice the kinetic contribution from the projectile charge  $q$ . Finally we have the smoothed total energy  $E_{total}$  in blue broken line with dots. On the right panel we show the Löwdin charge  $q$  evolution of the projectile as it advances.

The greatest advantage of this energy treatment is to have flat energy curve before and after the impact, thus facilitating the extraction of total energy variation  $\Delta E = E_{fin} - E_{init}$ . In the rest of this chapter, all atomic systems are treated by this technique to obtain the smoothed  $E_{total}$ . We can use this total energy directly for comparison between cases in

the absence and presence of the projectile basis. However, when we simulate different projectiles with projectile basis, the projectile charges would be different and so are the corresponding electron kinetic energies  $E_{kin}^q = qv^2/2$ . This quantity does not contribute to the target-projectile interactions and is merely a representation of the projectile charge. It thus introduces a bias to the comparison and need to be subtracted from  $E_{total}$ . The utility of this processing is better demonstrated later at section 5.2.4. At last, we recall that for solid systems the smoothing treatment is no longer interesting since we focus on the averaged slope of the energy curve rather than the absolute difference between the start and the end of the simulations (see figure 2.4.1).

## 5.2.2 Replace physical atoms by ghost sites

One basic requirement that the code should satisfy is to run the RT propagation correctly at the absence of target atomic cores while keeping the target basis functions. We name these atom-less sites “ghosts”. With this particular setup, we expect two quantities to be conserved:

- 1) The total energy of the system is not supposed to vary (apart from numerical noises) since no real interactions would happen between the projectile atom and the ghosts.
- 2) For the same reason, the total electron number of the system should be conserved.

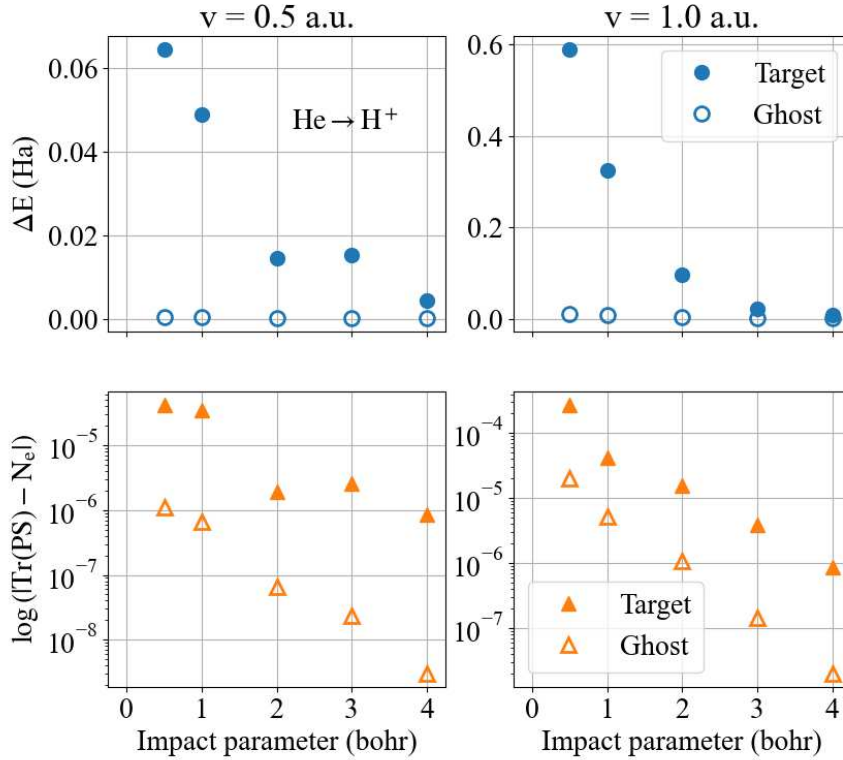
There are two ways to calculate the electron number  $N_e$  inside our code. We can either evaluate the trace of matrix product between the density matrix  $P$  and the overlap matrix  $S$ , or integrate the electron density  $\rho(\mathbf{r})$  in a real-space grid

$$N_e = \text{Tr}\{PS\} = \int d\mathbf{r} \rho(\mathbf{r}). \quad (5.2.2)$$

These two methods should lead to the same results or have infinitesimal difference.

Figure 5.2.2 compares the ghost sites against the real target for a system of He projectile and H target at  $v = 0.5$  a.u. (25 keV) and  $v = 1.0$  a.u. (100 keV). On the energy side, we see that in contrast to systems with a real target, the total energy barely varies in the presence of the ghost, resulting in an almost null  $\Delta E$  at both velocities. This confirms our first expectation. We also notice that for the real target, the total energy changes less as the impact parameter gets larger with an exception at  $v = 0.5$  a.u. for impact parameter  $p = 3.0$  bohr. We do not have a full explanation for this particular data point, but it seems

to reflect the projectile charge state as we shall see later in the next test. In terms of the electron number we report that it is well conserved for all cases and find it more pertinent to show the absolute difference between the two calculation methods mentioned in equation (5.2.2). We see that the agreement is extremely good at both velocities which indicates the healthy performance of the code in the presence of ghost sites.

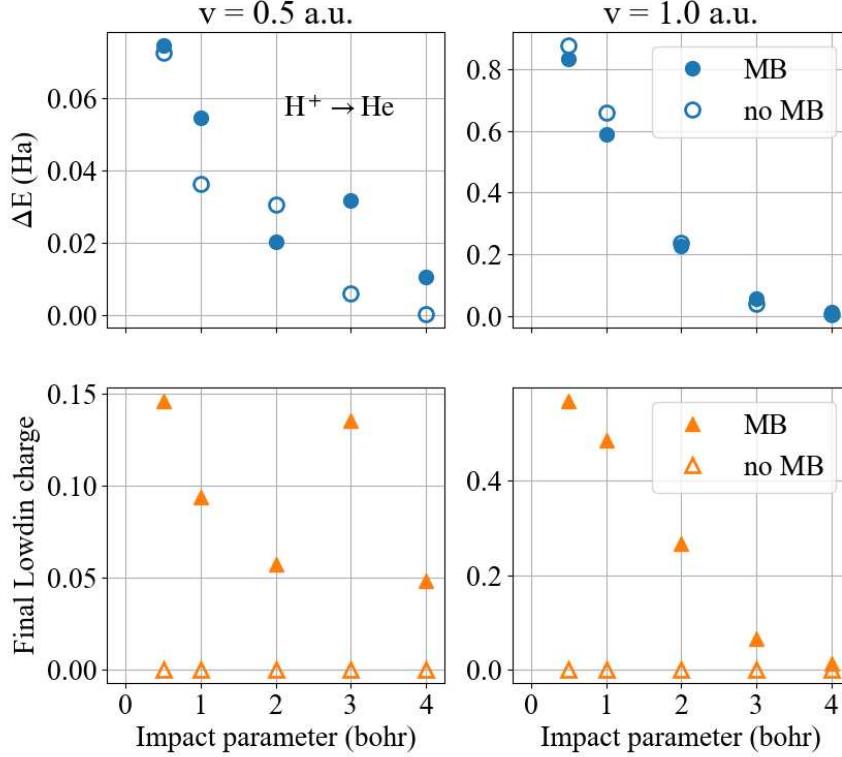


**Figure 5.2.2:** Projectile He (A6Z) with target or ghost H (A6Z). The upper panels show the total energy variation  $\Delta E$  of the systems. Empty blues dots represent results using a ghost and full blue circles represent results using a real target. The lower panels give the difference at log-scale between the two ways of total electron number  $N_e$  calculation in equation (5.2.2). Empty orange triangles show for system using a ghost and full orange triangles show for system using a real target.

### 5.2.3 Compare projectile with and without basis

When the projectile is light and has no initial electrons, like the proton, the addition of projectile basis is expected to give very similar energy results to that of a system without it. At the same time, the presence of basis functions allows the projectile to capture and keep electrons around it and might lead to some discrepancies between the two basis settings. Figure 5.2.3 confirms these beliefs for proton in isolated helium atom at two different velocities. In this figure, not only do we compare the energy variation  $\Delta E$  but we also

present the final Löwdin charge  $q$  on the projectile. This latter quantity is logically zero when no basis is used on the projectile, which we can see from the Löwdin results at both velocities.



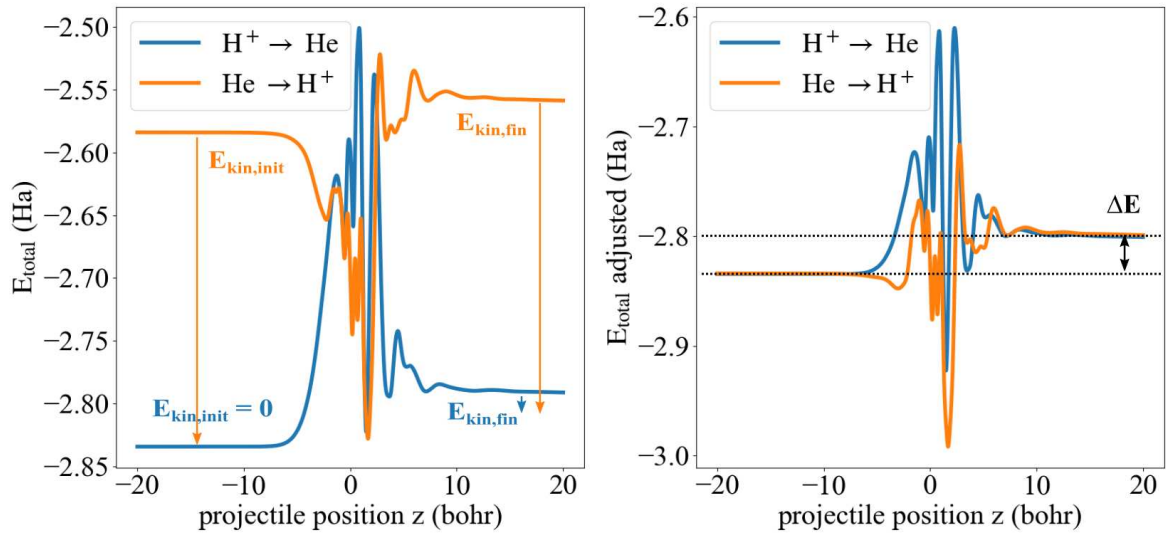
**Figure 5.2.3:** Presence and absence of projectile basis for proton (A6Z) in He (A6Z). The upper panels show the total energy variation  $\Delta E$  of the systems. Full blues dots represent results using moving projectile basis (MB) and empty blue dots represent results without MB (no MB). The lower panels give the final Löwdin charge on the projectile. Full orange triangles show for the MB system and empty orange triangles show for the no MB system.

At  $v = 0.5$  a.u. (6.25 keV),  $\Delta E$  experiences some large differences between the two basis settings. Similar to the exception observed in figure 5.2.2 at  $v = 0.5$  a.u. and  $p = 3.0$  bohr, while we cannot pinpoint the reason for the energy behavior, we certainly notice its similarity to the behavior of the final Löwdin charge on the projectile. Another way to explain the energy discrepancy between the two basis settings at  $v = 0.5$  a.u. is that since the projectile is moving rather slowly, it has enough time to exchange with the target and that their interactions are better described in the presence of projectile basis. The picture changes at  $v = 1.0$  a.u. (25 keV) and the agreement on  $\Delta E$  is much stronger between the two settings. In terms of the final Löwdin charge, we also notice that more is captured by the projectile at higher velocity since the impact energy is greater and can produce stronger interactions.

The comparison between the two basis settings shows us the potential improvements that projectile basis can bring to the stopping power simulations. By allowing the transfers of electronic charge between the target and the projectile, we aim to capture their interactions with better precision than the previous development of Maliyov *et al.* [48, 49] done without the projectile basis.

### 5.2.4 System's symmetry test

Another important requirement the code should fulfill is to properly handle the switching of roles between the target and the projectile in a diatomic system. These two scenarios are supposed to give the same  $\Delta E$ . In figure 5.2.4 we demonstrate this feature for two equivalent systems composed of a proton and a helium atom. The target is placed at  $z = 0$  with an impact parameter  $p = 1.1$  bohr, and the total energy  $E_{total}$  on the left-side image is treated by the smoothing technique presented in figure 5.2.1. The two energy profiles are completely different at this stage.



**Figure 5.2.4:** Role-switching test between H (A6Z) and He (A6Z). On the left side are the total energy curves for the two systems  $H^+ \rightarrow He$  (in blue) and  $He \rightarrow H^+$  (in orange). The arrows with matching colors indicate the subtraction of kinetic energy of projectile electrons from the corresponding energy curves. On the right side are the energy curves after adjustments and the  $\Delta E$  is indicated by the black double arrow.

We have mentioned in section 4.2.1 that for comparison between two different projectiles using projectile basis, the kinetic contributions of the projectile charges should be taken out from the total energy. Knowing the real-time Löwdin charge  $q(t)$  as calculated in equation

(5.2.1), we can easily estimate the corresponding kinetic energy at each time step

$$E_{kin}^q(t) = \frac{v^2}{2}q(t), \quad (5.2.3)$$

where  $v$  is the projectile velocity. For the pair of role-switching systems,  $E_{kin}^q$  is obviously different right from the beginning as the two projectiles initially possess different amount of electrons. Subtracting  $E_{kin}^q$  from  $E_{total}$  eventually superposes the two energy curves at the initial and the final states and gives two identical  $\Delta E$ . This signifies that the energy transfer happens correctly within both systems.

Around  $z = 0$ , the two energy profiles are still remarkably different even after the subtraction of  $E_{kin}^q$ . In this area where the two atoms encounter, the detailed description of the complex dynamics requires the calculation of the force corrections as stated in the work of Kunert and Schmidt [103] which is not available in MOLGW. However, this does not affect the calculation of  $\Delta E$  because the consequences of the target-projectile interactions are in the final energy once the projectile leaves the impact zone. Therefore the conclusions that we have drawn from figure 5.2.4 are still valid.

Passing all of the three tests mentioned above is a solid proof that our implementations function soundly within MOLGW and that our code is ready to be applied to complex systems like the solid clusters. In the next chapter we will analyse the results obtained with moving projectile basis for different projectiles in both lithium and aluminum targets.

# Chapter 6

## Electronic Stopping Power with Projectile Basis in Li and Al

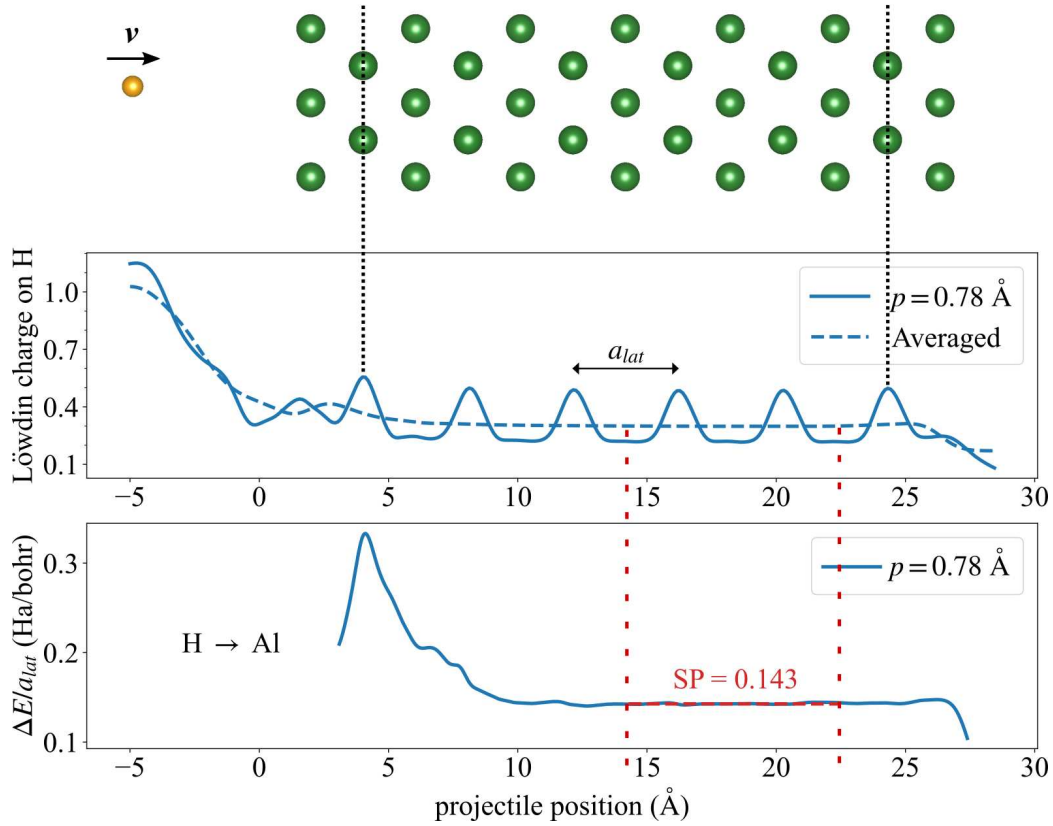
In this chapter we focus on the simulations carried out in solid systems with light to medium projectiles in the presence of projectile basis. The first section demonstrates the convergence tests done with two major groups of parameters: the cluster geometry and the basis quality. Cluster length and radius will be discussed under the topic of the geometry, and the basis quality concerns both the target and the projectile. Afterwards we will first study the random electron stopping power (RESP) of hydrogen and helium in lithium which are relatively light systems for the computation. Then we will have a look at the channeling SP of these two projectiles in aluminum before moving on to the RESP results in aluminum. Finally, apart from the two light projectiles mentioned above, aluminum is used as our first heavier projectile with core electrons and its RESP inside the aluminum target will be examined.

### 6.1 Convergence Parameters

In numerical simulations many parameters are used to define the conditions under which the systems exist and the phenomena take place. The outcomes of the calculations and the convergence of results depend heavily on the quality of these parameters. The two main sets of parameters in our study that require specific attention are the cluster geometry and the basis quality. Given the crystal structure and orientation, length and radius are the two major factors determining the cluster geometry. On the basis quality side, target and

projectile basis each plays a role to converge the results.

We admit here that at the beginning of our work these parameters are chosen based on less thorough convergence studies, and the more rigorous tests given in this section come at a much later stage. Since most calculations are carried out with the less ideal parameters and are very expensive to relaunch (at least 8 months of human time required), we decide to be consistent and present all our stopping power results using the old parameters later in this chapter. The conclusions drawn from the convergence tests in this section can therefore be considered as recommendations for future endeavours.



**Figure 6.1.1:** Löwdin charge stabilization and the averaged SP of hydrogen (DZ basis) in fcc [001] aluminum (ACQZ/DZ/DZ) at  $v = 3.0$  a.u. and  $p = 0.78$  Å. The system is illustrated in the upper panel with hydrogen represented by an orange sphere and aluminum by green spheres. The two black vertical dotted lines indicate the first and the last planes of atoms closest to the projectile trajectory. In the middle panel we show the Löwdin charge profile as the projectile enters into the cluster. The real-time evolution is traced by a blue solid line and the running average value traced by a blue broken line. The lattice constant  $a_{lat} = 4.05$  Å is indicated by a double-headed arrow between two charge peaks. In the bottom panel illustrates the averaging technique for the single-trajectory SP. The blue solid line traces the running SP and the red horizontal broken line indicates the averaged SP value within the sampling zone delimited by the two red vertical broken lines.

A technique was mentioned in section 4.1.3 which uses SCF cycles to accelerate the

initial stabilization of moving projectile with the effective Hamiltonian  $\hat{M} = \hat{H} - i\hat{D}$ . Unfortunately the same cannot be applied to the solid systems since the SCF cycles are difficult to converge due to the energy shifting of orbitals and the orbital mixing between the target atoms and the projectile. The system is thus left to find a new stationary state while the projectile advances. To buffer this transition phase we are required to adopt very lengthy clusters. Figure 6.1.1 demonstrates this early transition phase by showing how the averaged Löwdin charge on the hydrogen projectile stabilizes inside an aluminum cluster after progressing through a few Angstroms.

Like the energy profile in figure 2.4.1, the Löwdin charge also shows a peak periodically whenever the projectile has a close encounter with a target atom. A simple running average technique is applied to obtain the averaged Löwdin charge. First we divide the entire distance  $z$  travelled by the projectile into a grid of steps  $dz$ , this gives us  $n = z/dz$  data points. Since we have a periodic structure, it is more intuitive to sample the mean over the lattice constant  $a_{lat}$ . The data size of the sampling window is thus  $k = a_{lat}/dz$  and the mean inside such a window is

$$\langle q \rangle_k = \frac{1}{k} \sum_{i=1}^k q_i. \quad (6.1.1)$$

Next we “slide” the window by one data point and calculate the next mean

$$\langle q \rangle_{k,next} = \frac{1}{k} \sum_{i=2}^{k+1} q_i. \quad (6.1.2)$$

Repeating this procedure until the end of data produces the averaged trend in the middle panel of figure 6.1.1.

One thing worth mentioning is that the stopping power does not seem to depend on the initial charge state of the projectile, given that the target is sufficiently long for the projectile to find a steady state [77, 107, 108]. Judging from the stable averaged charge in figure 6.1.1, the clusters used in our study are long enough (above 20 Å) to neglect effects caused by the initial charge state. It has also been reported by references [108] and [109] that initially neutral projectiles reach charge stabilization faster than initially charged ions. Therefore, all our calculations in solids presented in this chapter involve initially neutral projectiles.

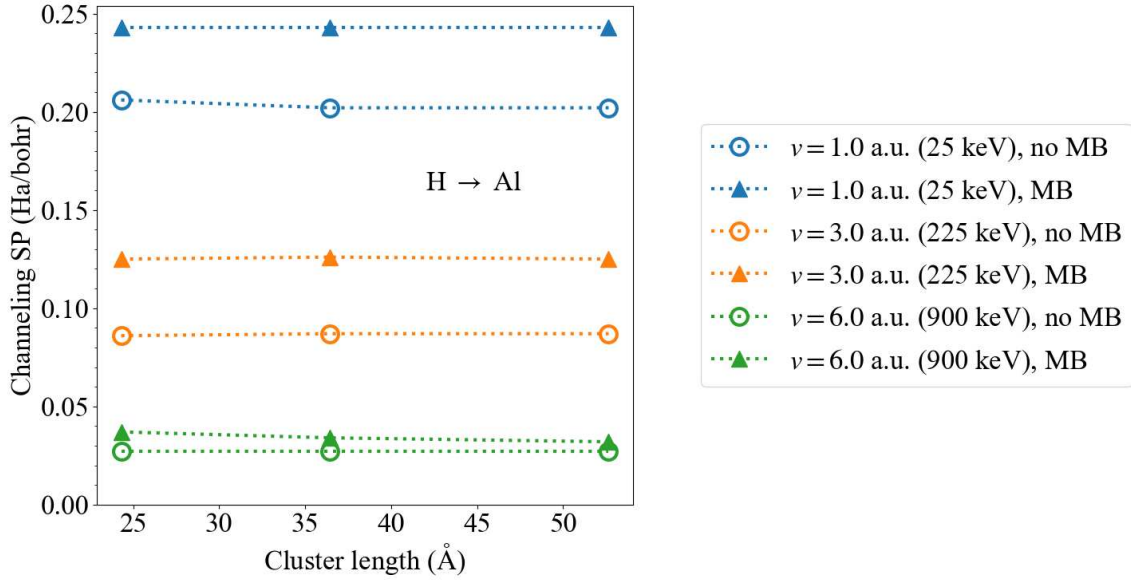
Usually the stabilization of the charge is a good indicator for the stabilization of the stopping power. In practice we will first calculate the running SP which is the total energy

difference between lattice constants normalized by the lattice constant  $[E(z + a_{lat}) - E(z)]/a_{lat} = \Delta E/a_{lat}$ . Once the steady state has been reached, the energy loss becomes a periodic function of the crystalline structure and  $\Delta E/a_{lat}$  becomes constant. Then we obtain the definitive SP which is the averaged running SP over the distance travelled inside the stabilization zone. An illustration of such sampling can be found in the lower panel of figure 6.1.1.

There is one more comment on the stabilization. Unexpectedly, sometimes the stopping power are observed to stabilize much slower than the Löwdin charge. In order to ensure the convergence, the optimal length of the clusters need to be discussed. Meanwhile, to mimic the electron density of the bulk and avoid passing the projectile too close to the surface, we need to control the radius of the clusters.

### 6.1.1 Cluster geometry - length

Let us first focus on the length. Figure 6.1.2 give us detailed information about the SP convergence of hydrogen in aluminum for three different lengths (24 Å, 36 Å and 53 Å) under the channeling condition ( $p = 1.43$  Å). Three velocities are studied namely 1.0 a.u. (25 keV), 3.0 a.u. (225 keV) and 6.0 a.u. (900 keV), and the presence (MB) and the absence (no MB) of the projectile basis are compared. We notice that the channeling SP is almost converged at the length of 36 Å for all velocities, with or without projectile basis. There is still a slight descending trend at  $v = 6.0$  a.u. which corresponds to a tolerable difference of 5% between the 36 Å and 53 Å-long cluster.



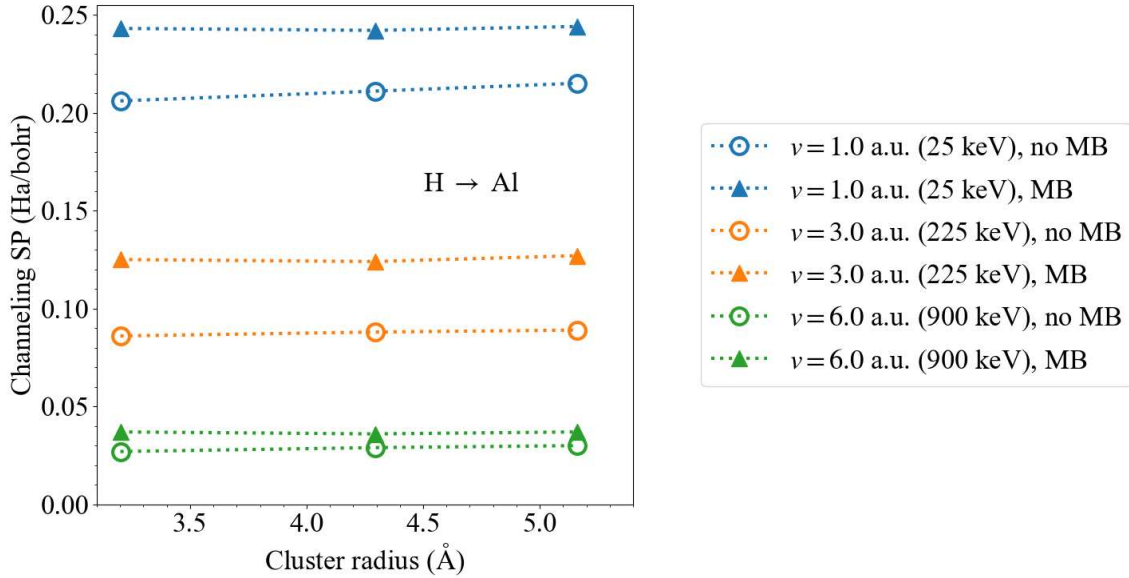
**Figure 6.1.2:** Channeling SP in relation to lengths for hydrogen (DZ) in fcc [001] aluminum (ACQZ/DZ/DZ) at different velocities with (MB) and without (no MB) projectile basis. Results from the three velocities 1.0, 3.0 and 6.0 a.u. are indicated by colors blue, orange and green respectively. No MB simulations are marked by empty circles and MB simulations by triangles.

Ideally we would set the length of aluminum cluster at 36 Å for future calculations. However, the human time required for a single-trajectory simulation at a given velocity in a cluster of 36 Å long is about 10 hours more than that in a cluster of 24 Å long which takes in average 24 hours. This would scale up quickly for all the velocities and random trajectories as well as the different systems to be studied. Since many of our calculations in aluminum precede this convergence test and are carried out with the length of 24 Å, we decide to be consistent and continue using this length for aluminum in the rest of this thesis.

### 6.1.2 Cluster geometry - radius

Now we look at the influence of cluster radius on the channeling SP convergence in figure 6.1.3 and the three radius studied are 3.2 Å, 4.3 Å and 5.2 Å. For simulations done with projectile basis (MB), the convergence is reached much faster than the no MB setting at all velocities, and the difference between the smallest and the largest radius does not exceed 2.5%. For simulations done without projectile basis (no MB), while the ascending trend at  $v \leq 3.0$  a.u. results in a 5% difference between the smallest and the largest radius, this difference surpasses 10% at  $v = 6.0$  a.u.. The slower radius convergence of the no MB

calculations indicates by contrast an advantage in the MB setting where much thinner clusters can be considered.



**Figure 6.1.3:** Channeling SP in relation to radius for hydrogen (DZ) in fcc [001] aluminum (ACQZ/DZ/DZ) at different velocities under the channeling condition with (MB) and without (no MB) projectile basis. Results from the three velocities 1.0, 3.0 and 6.0 a.u. are indicated by colors blue, orange and green respectively. No MB simulations are marked by circle and MB simulations by triangles.

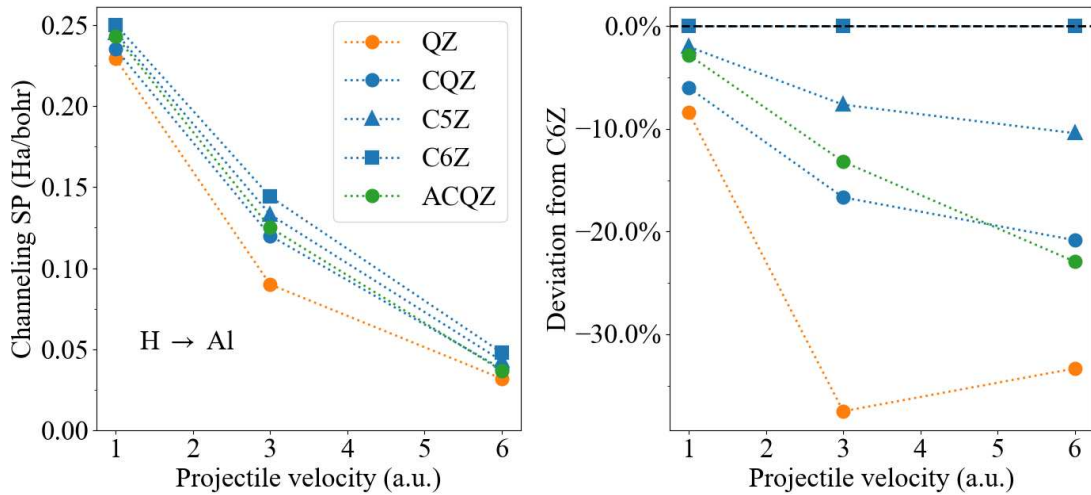
Combining this observation with the conclusions from the length convergence test, an ideal geometry of the aluminum cluster would be 36 Å in length and 3.2 Å in radius. However, as explained previously, an aluminum cluster of 24 Å in length and 3.2 Å in radius is used instead for the rest of this work due to the fact that most of our calculations are conducted before the presented convergence tests.

### 6.1.3 Basis quality - target

We recall from chapter 2.2 that the quality of the Dunning basis sets are defined by both the cardinal number  $X$  and the basis extension. Starting from the standard  $XZ$  basis, we can augment to diffuse  $AXZ$  basis, core-valence  $CXZ$  basis and diffuse core-valence  $ACXZ$  basis. For systems void of projectile basis, the work of Maliyov *et al.* [49] has demonstrated systematic convergence when raising the target basis quality by both the extension level and the cardinal number. This feature has eventually led to their basis set optimization technique with the objective to converge on the stopping power. The complexity of the SP convergence comes with the addition of projectile basis. We have observed that the

quality of basis used on each part can influence the results in different ways, making the convergence trend very hard to capture. Figure 6.1.4 and 6.1.6 resume this problem and show how the stopping power is affected by either the target or the projectile basis quality. Here we apply the mixed basis technique introduced in section 2.2 and vary the basis quality only on the target atoms within the closest impact distance from the projectile. The outer layers of target atoms all use the DZ basis sets.

To study the target basis convergence we have chosen the system of hydrogen in aluminum under the channeling condition ( $p = 1.43 \text{ \AA}$ ). The three velocities 1.0, 3.0 and 6.0 a.u. correspond to the hydrogen kinetic energies of 25, 225 and 900 keV. On the left-hand side of figure 6.1.4 we report the stopping power values for different target basis and notice immediately that C6Z gives the highest SP at all velocities. On the right-hand side of the figure we show the deviation of SP values from results obtained with the C6Z basis.



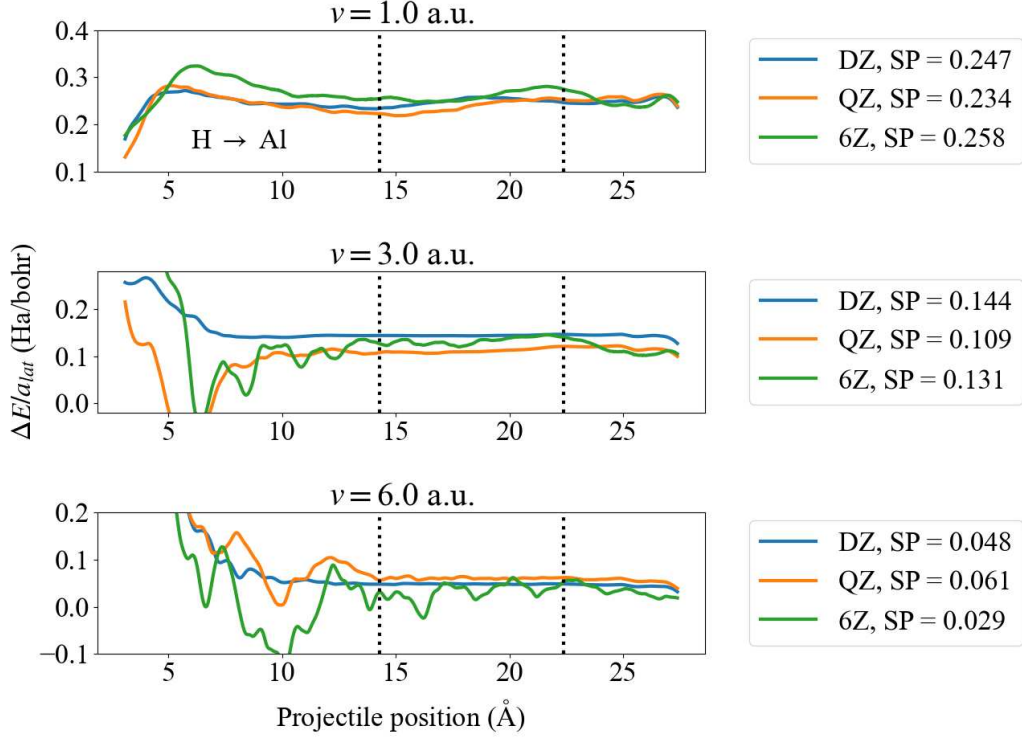
**Figure 6.1.4:** Convergence of channeling SP of hydrogen in relation to target basis quality in aluminum at different velocities. The circles mark for QZ, CQZ and ACQZ basis using orange, blue and green colors respectively. The blue triangle and squares represent results from C5Z and C6Z basis. On the left-hand side we show the channeling SP values for each basis set, and on the right-hand side we compare these values to those of the C6Z basis set in terms of percentage of deviation.

We can breakdown the analysis into two control groups. First let us compare the effects of basis extension amongst QZ, CQZ and ACQZ. While it is obvious that QZ is under-performing dramatically as velocity goes up, CQZ and ACQZ stay very close together within an interval of 5%. This gives us a hint that the CXZ group might be the best basis extension to use, with ACXZ being the second best at the cost of larger computational efforts. Next we look at the cardinal number  $X$  within the group CXZ and observe a

systematic increase as  $X$  goes up, which agrees with the findings in Maliyov’s work [49]. While at  $v = 1.0$  a.u. the increase in SP tends to slow down from CQZ to C6Z, it is not the case for  $v \geq 3.0$  a.u.. Combining both the basis extension and the cardinal number, we believe that higher-order CXZ basis are needed to reach convergence, especially at higher velocities. However, such heavy basis would require expensive calculations. For example, the difference in computer time between the calculations using CQZ and C6Z target basis is almost 3000 hours using 288 CPU cores on Irene Skylake [110]. Due to the limits in computational resources and human time, we will be contented to use either the CQZ or ACQZ target basis in most of the studies presented later in this chapter. The results of our simulations are thus more qualitative than quantitative while providing a general understanding of the SP and RESP behaviors.

#### 6.1.4 Basis quality - projectile

Now we will look at the influence of projectile basis quality on the stopping powers. It is more informative to divide the analysis into two cases depending on whether the projectile possesses core electrons. For light projectiles like hydrogen and helium who only have valence shells, no CXZ basis sets are constructed in the Basis Set Exchange database [61, 60]. Therefore we focus on the comparisons within the standard basis group  $XZ$ .

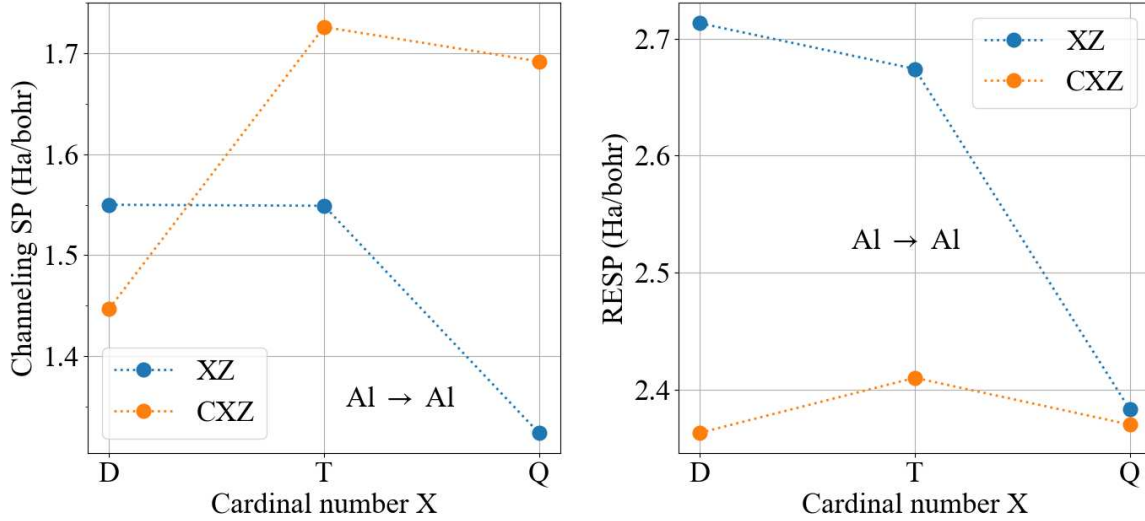


**Figure 6.1.5:** Running SP of hydrogen in fcc [001] aluminum (C6Z/DZ/DZ) with different projectile basis  $XZ$  at  $v = 1.0, 3.0$  and  $6.0$  a.u. under the channeling condition. Results from the DZ basis are reported with a blue line, QZ with an orange line and 6Z with a green line. The averaged values of the channeling SP for each basis are given in the legend boxes.

Figure 6.1.5 shows the running stopping power  $[E(z + a_{lat}) - E(z)]/a_{lat}$  for hydrogen in aluminum under channeling conditions at three velocities  $v = 1.0, 3.0$  and  $6.0$  a.u.. Recall that we have established in the target basis convergence study that high-order  $CXZ$  basis are required for the targets. Hence we have used C6Z for the Al target in this study. We then vary the basis cardinal number  $X$  on hydrogen and observe the following features. First, the results given by both DZ and QZ are stable at all velocities, while the results of 6Z are stable only at  $v = 1.0$  a.u. and oscillate more and more as  $v$  becomes greater. Second, there is no obvious convergence of the averaged SP, and it can be either increasing or decreasing as we raise the cardinal number  $X$ . At last, combining the computational costs with the stability of results, it is the most efficient for us to use the DZ basis set on light projectiles.

For heavier projectiles like aluminum which possess both valence and core electrons, it makes more sense to use the  $CXZ$  basis sets. Figure 6.1.6 gives both the channeling SP and the RESP for aluminum in aluminum at  $v = 2.0$  a.u. (2.7 MeV). The basis set used on the central target atoms is CQZ in order to save computational efforts. What makes

it interesting to examine the RESP convergence beside the channeling SP is that we can factor in the geometric weights of single trajectories and understand the impact of their individual errors.



**Figure 6.1.6:** Convergence of both channeling SP (left-hand image) and RESP (right-hand image) of aluminum in fcc [001] aluminum (CQZ/DZ/DZ) as a function of the projectile basis quality at  $v = 2.0$  a.u.. The blue-colored circles mark the results from the standard XZ basis and the orange ones represent results from the core-valence CXZ basis. The left-hand side image shows the channeling SP values for different projectile basis, and the right-hand side image compares the RESP values.

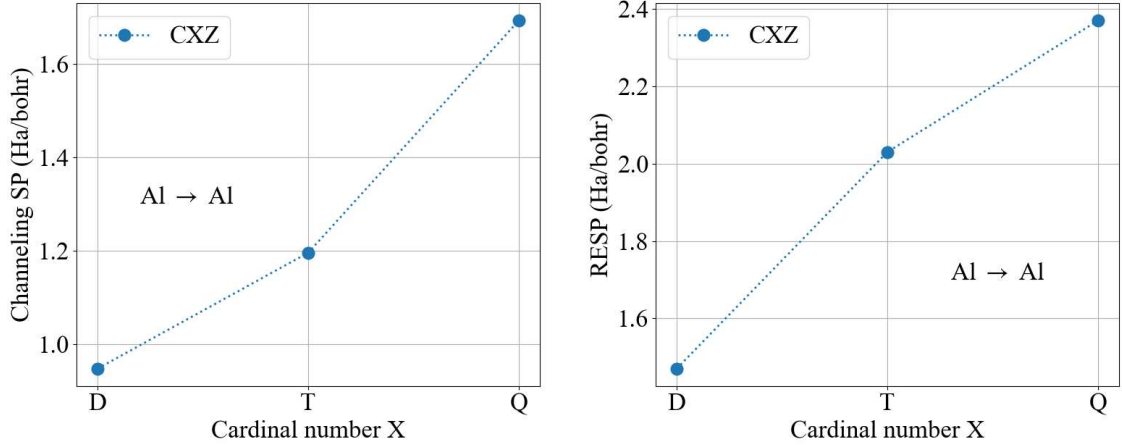
Starting with the standard XZ basis in figure 6.1.6. From DZ to TZ the channeling SP value stays stable and then decreases about 14% with the QZ basis. A similar trend is observed at the RESP where the drop in values is approximately 10% from TZ to QZ. Before we compare the standard basis to the CXZ basis, let us examine the latter separately. For the channeling simulations, the increase in the cardinal number  $X$  entails a sharp increase in SP of roughly 20% at CTZ then a slight drop of 2% at CQZ. This peak at CTZ persists for the RESP, where the value increases much more gently with 2% from CDZ to CTZ and goes back down 2% from CTZ to CQZ. The difference between the channeling SP and the RESP highlights the partiality of information given by the single trajectories. At the same time the similarity in their trends proves that important insights can be gained from single-trajectory studies.

We now compare between the two groups of basis sets. Looking at the channeling SP, including core electron contribution with the CXZ basis introduces an initial drop of 7% at  $X = D$ . The SP value of CTZ then surpasses TZ by 11% and the value of CQZ is 27%

higher than that of the QZ basis. Moving on to the RESP, we notice that the two groups of basis sets have completely different trends. While CDZ gives significantly lower value than the DZ basis, the gap between the two groups reduces as  $X$  becomes larger. At  $X = Q$  the value calculated with QZ is at the same level as that of the CQZ basis. This lead us to believe that the convergence is reached for the RESP with the QZ and CQZ basis sets. Taking into account of the smoother channeling SP evolution within the CXZ group than the XZ group, CQZ seems to be the most suitable candidate for projectile basis.

All things equal, the extra human time required in calculations for raising one level of cardinal number  $X$  on the projectile basis is at least 2 hours. About the same amount of time is needed for passing from XZ to CXZ projectile basis at equal cardinal number. Typically one single-trajectory calculation consumes 288 CPU cores on Irene Skylake [110] and 17 hours with DZ projectile in a CQZ/DZ/DZ target. This counts for nearly 5000 computer hours and would add up quickly when multiplying the number of simulations. Since the computational resources granted to us are limited, we have decided not to carry out further analysis with higher orders of  $X$ , and will use the CDZ basis instead of the CQZ basis on the projectile to save machine costs. With this decision, the results that we obtain become more qualitative than quantitative and we encourage future studies to use higher order CXZ basis on projectiles for better convergence.

There is one more case worth investigating before we end this section. In a particular system where the projectile and the target are the same atoms, like aluminum in aluminum, it might be sensible to apply the same basis on both parts. Figure 6.1.7 demonstrates the results from this investigation. We have chosen the CXZ basis sets based on the target basis convergence test where we have observed the importance of the core electron expansion (C). While the channeling SP seems far from converged in figure 6.1.7, as the distance between CTZ and CQZ gets larger than that between CDZ and CTZ, the RESP shows a slow-down in the ascending trend as  $X$  rises. Constrains in time and machine resources have discouraged us from examining higher  $X$  values during this work, but it would be a subject worthy of future endeavours.



**Figure 6.1.7:** Convergence of channeling SP (left image) and RESP (right image) in case of identical CXZ basis settings on both the projectile and the target for aluminum in fcc [001] aluminum. The value of  $X$  varies from double (D) to quadruple (Q).

In this section we have presented various convergence studies in order to assure the stabilization of energy variation  $\Delta E/a_{lat}$  which is crucial to the convergence of the stopping power results. The two major groups of modeling parameters influencing the simulation outcomes are the cluster geometry and the basis quality. Under the topic of cluster geometry, the length and radius of the clusters are discussed and we have noticed the difference in sensitivity between the MB and the no MB calculations. In terms of the basis quality, both the target and projectile basis are considered with the latter depending also on the electron configuration of the projectile. Apart from the convergence tests presented, there are a few factors that we have not covered including the crystal orientation of the cluster and the number of impact parameters sampled for the RESP averaging in equation (2.4.13). Our decisions concerning these two factors are therefore based on the convergence analysis in references [72, 46] for the no MB simulations which show little sensitivity. It would probably be beneficial for the future studies to test these factors also on the MB calculations.

Having concluded on the convergence studies, we now move on to the simulations of channeling and random electron stopping powers for several pairs of projectile and target in the following sections.

## 6.2 Random Electron Stopping Power in Lithium

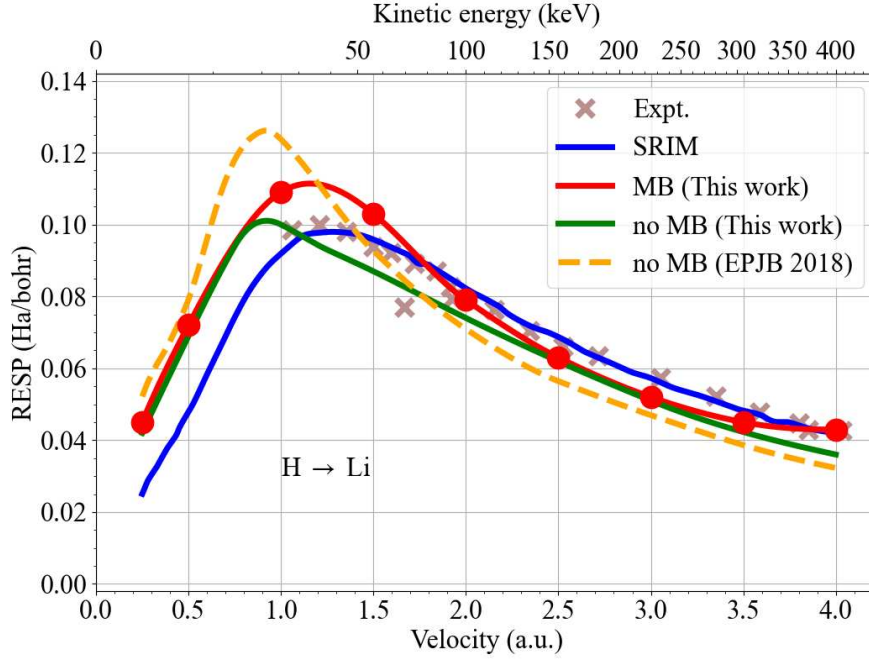
Let us first study the random electronic stopping power (RESP) with the simplest metal target on the periodic table, lithium. Thanks to the only three electrons that it possesses, the size of its basis and the number of occupied states  $N_{OCC}$  are relatively smaller than those of aluminum. This grants us smaller matrices like  $H$ ,  $C$  and  $S$  and the computational advantage of employing larger clusters. At their most stable forms the lithium metal has a body-centered cubic (bcc) structure and the aluminum metal is a face-centered cubic (fcc) crystal. The geometry of the lithium cluster at direction [001] is therefore slightly different from that of the aluminum due to the difference in crystal structure. On top of that, the lithium crystal has a lattice constant of  $a_{lat} = 3.49 \text{ \AA}$  and the aluminum crystal has  $a_{lat} = 4.05 \text{ \AA}$ , which causes more differences in their cluster dimensions.

Since the calculations in lithium have been completed before the more systematic convergence tests conducted for aluminum in section 5.1, the geometry and basis parameters used are not necessarily the optimal concerning the costs and accuracy, but are still chosen in a way to ensure good basis completeness and energy stabilisation without excessive computational efforts. The results shown in this section are obtained with a cluster of 35  $\text{\AA}$  in length and 10  $\text{\AA}$  in diameter which contains 134 lithium atoms in total. The basis mixture on the target atoms is CQZ/DZ/DZ and the projectiles are described with the TZ basis set. In the spirit of starting with simple systems, only light projectiles such as hydrogen and helium are simulated inside lithium. One more detail to mention is that the sampling scheme for the impact parameters  $p$  in lithium is carried out with the previous polar symmetry method of Maliyov and coworkers [48] as illustrated in figure 2.4.2 instead of the newly developed angled sampling technique in figure 2.4.3.

### 6.2.1 Hydrogen in lithium

The first projectile we analyse is hydrogen. Figure 6.2.1 reports the random electronic stopping power of hydrogen in lithium for projectile velocities ranging from 0.25 a.u. (1.6 keV) to 4.0 a.u. (400 keV). Apart from results obtained by our own calculations with moving projectile basis (MB), we also cite in the same figure some other sets of results:

simulations done under the same conditions as MB except without the projectile basis (no MB), results from Maliyov *et al.* [48] obtained without projectile basis (no MB) using the MOLGW program, empirical prediction from the SRIM online database [18] and a collection of historical experimental data [111, 112].



**Figure 6.2.1:** RESP of hydrogen in bcc [001] lithium at different velocities. The experimental data [111, 112] are marked by the brown crosses and the SRIM prediction is given by the blue solid line. The results from our calculations using TZ as projectile basis and CQZ/DZ/DZ as target basis are represented by the red solid line with round markers. The no MB results calculated under the same parameters are drawn with the green solid line and the no MB results from Maliyov’s work [48] using MOLGW are plotted with the orange broken line.

We would like to point out the two major differences in setups between the two series of no MB calculations. One is the cluster geometry. The lithium cluster used in Maliyov’s work is shorter in length (7 Å) and larger in diameter (14 Å) and contains 62 atoms. More detailed explanations of the choice of geometry parameters can be found in the thesis of Maliyov [72], section 3.1.2. At the same time we recall from our own geometry convergence analysis in figure 6.1.2 and 6.1.3 that simulations without projectile basis tend to converge faster in length and slower in radius comparing to that of MB. It is thus not surprising that such a thin and wide cluster shape is selected by Maliyov’s study. Apart from the geometry, the target basis mixture is slightly different between Maliyov’s (ACQZ/TZ/DZ) and our (CQZ/DZ/DZ) calculations. However, as discussed previously in the basis mixture (figure 2.2.1) and the target basis (figure 6.1.4) convergence analysis, using the CXZ

basis set rather than its more diffused version ACXZ and changing the second-layer basis quality from TZ to DZ should not alter significantly the stopping powers. Nevertheless, the multiple variations in the modeling parameters cause the disagreement between the two sets of no MB results and make it less informative to compare our MB results to the work of Maliyov and coworkers. Therefore from this point on we will only refer to the no MB results obtained under the same modeling conditions as our MB calculations.

Coming back to figure 6.2.1, we would like to first comment on the consistency between the experimental data [111, 112] and the SRIM prediction. These experiments are cited by the SRIM program as data source for fitting and scaling [18, 19]. While information from experiments is abundant for velocities above 1 a.u., there seems to be no experimental records at lower velocities. This leads to a higher confidence level in the SRIM prediction at higher velocity region where it fits accurately the experimental data, and much less confidence in the lower velocity region due to the absence of experimental evidence.

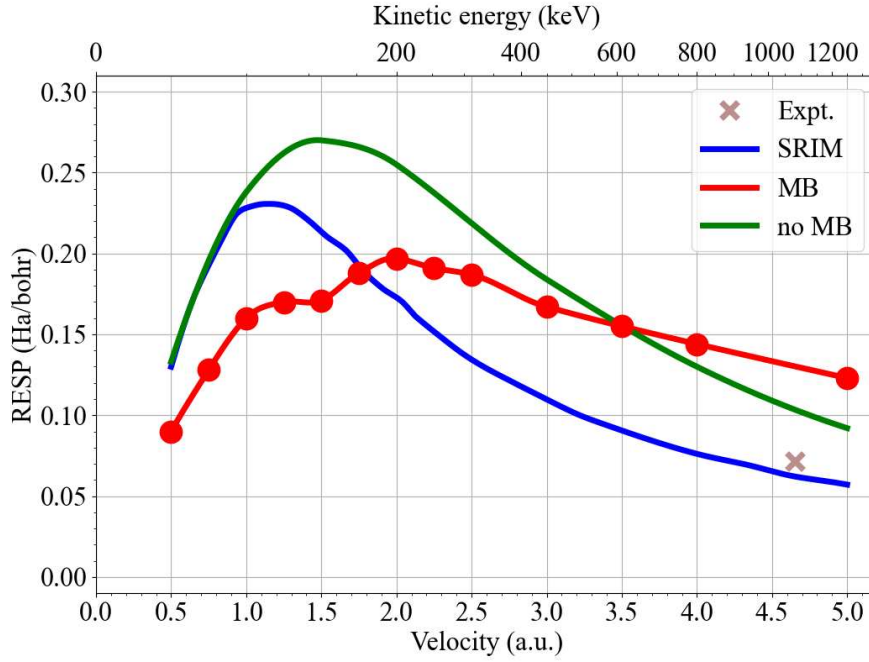
Now let us move on to compare the no MB results from this work to that of the SRIM prediction. With a similar trend to SRIM, the no MB curve peaks at a velocity slightly below 1 a.u. before the SRIM peak. In terms of absolute values, the no MB curve from this work gives higher values at low velocities before diving under the SRIM curve after  $v = 1.0$  a.u.. The size of the gaps between these two curves before and after the cross-over point seem identical. This makes the difference between them look like a simple shift in peak position.

On the other hand when comparing the MB results to SRIM, we notice that the peaks are at the same velocity which is higher than that of the no MB peak. Like no MB, the MB curve follows the same ascending trend above the SRIM curve before dropping below it. The cross-over happens after  $v = 1.5$  a.u. which is at a higher velocity than that between the no MB curve and the SRIM curve. Finally from  $v = 3.0$  a.u. onward the descend of the MB curve slows down, leading the SP values to catch up with that of the SRIM prediction at  $v = 4.0$  a.u.. This strange behavior might be the consequence of less converged values at higher velocities regarding the length of the cluster or the completeness of the basis sets.

Overall, the MB curve has a normal ascending then descending form and gives values close to those of the experimental data. In addition, the peak position of the MB curve is much more accurate than that of the no MB curve, which is a noticeable improvement.

### 6.2.2 Helium in lithium

The second light projectile used in the lithium cluster is helium. Figure 6.2.2 gives the results calculated both with (MB) and without (no MB) projectile basis for velocities ranging from 0.5 a.u. (25 keV) to 5.0 a.u. (2.5 MeV). The benchmark data sets are the experimental data [113] cited by the SRIM database and the prediction from the SRIM method [18].



**Figure 6.2.2:** RESP of helium in lithium at different velocities. The experimental data [113] is marked by the brown cross and the SRIM prediction is given by the blue solid line. The results from our calculations using TZ as projectile basis and CQZ/DZ/DZ as target basis are represented by the red solid line with round markers and the no MB results calculated under the same parameters are traced by the green solid line.

One remarkable flaw in this figure is the poor collection of experimental data. In fact only one data point [113] is cited by the SRIM database [18], and the method has still managed to produce a complete curve for the whole range of velocities that we studied. While amazed by the predictive capacity of the SRIM method, one cannot help to wonder about the viability of this single experimental data and the reliability of the poorly based prediction.

Nonetheless, accepting the SRIM results as reference, we now compare them to the no MB calculations. Surprisingly those two curves are very similar in shapes. While the SRIM data suggest a peak right after  $v = 1.0$  a.u. (100 keV), the no MB curve peaks at

a faster  $v = 1.5$  a.u. (225 keV). In terms of the absolute values, the no MB results are almost in superposition with those of SRIM before  $v = 1.0$  a.u. and then surpass the latter significantly by 70% at their largest difference.

The MB results show a completely different trend than both the no MB and the SRIM results. Not only does the MB curve ascends and descends at rates slower than the other two curves as a function of the velocity, it also produces a shoulder at  $v = 1.25$  a.u. (160 keV) next to the peak at  $v = 2.0$  a.u. (400 keV). The absolute values of the MB curve are considerably lower than the no MB curve until their cross-over at  $v = 3.5$  a.u. (1.2 MeV). At the same time when comparing to the SRIM curve, the MB curve is under it before  $v = 1.75$  a.u. (300 keV) then stays well above the former at higher velocities. We have not yet understood these unusual behaviors of the MB results. While it could be an interesting topic for the future studies, it would also be important for the purpose of validation to acquire more experimental data of this particular system at lower velocities, especially at which the shoulder appears.

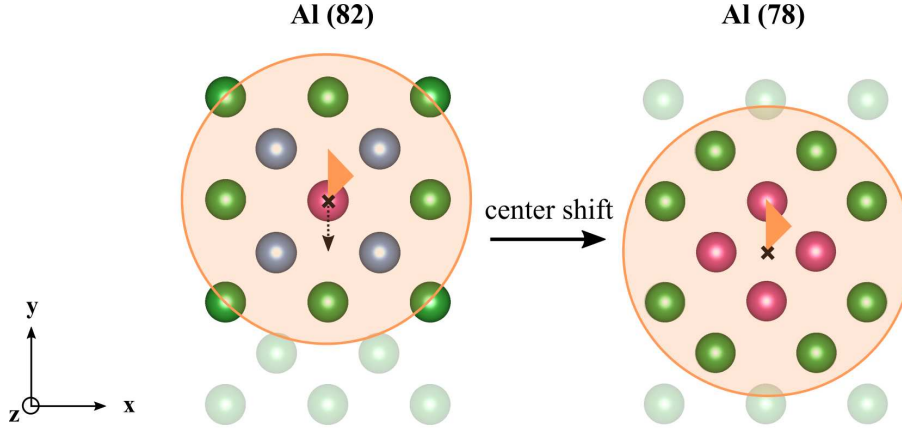
Despite of the unexpected observations about the helium RESP where no experiments can support the findings, we are well encouraged by the good results obtained with the hydrogen projectile and have decided to move on to a heavier target which is aluminum. The sections below will first talk about the channeling stopping powers of hydrogen and helium before moving on to the random trajectories in aluminum.

## 6.3 Channeling Stopping Power in Aluminum

Our most intensive investigation of channeling SP has been realized during the study of aluminum target. Therefore we will first look at the channeling condition in aluminum in this section before diving into the random trajectories in aluminum. As mentioned in Chapter 2, the channeling is a special experimental condition where the orientation of the mono-crystal is controlled in a way that the impinging ion enters without colliding head-on into the target atoms [38, 84]. Although in reality most materials are not mono-crystal and that the projectile may travel randomly inside the target, the channeling study is still a useful tool to gain insights on the velocity dependency of the stopping power.

In this section we study two projectiles, hydrogen and helium, impinging the fcc aluminum target oriented at [001]. The cluster size conforms to the geometry convergence

which is  $24.3 \text{ \AA}$  in length and  $6.4 = 2 \times 3.2 \text{ \AA}$  in diameter. The target basis used is ACQZ/DZ/DZ and the projectile has a DZ basis set. Again, this choice of basis quality is established before the more systematic basis convergence tests in sections 5.1.3 and 5.1.4, thus it does not follow our recommendation about the projectile basis being CDZ. Nevertheless the results that we have obtained give very good qualitative information as we shall see in the following sections.

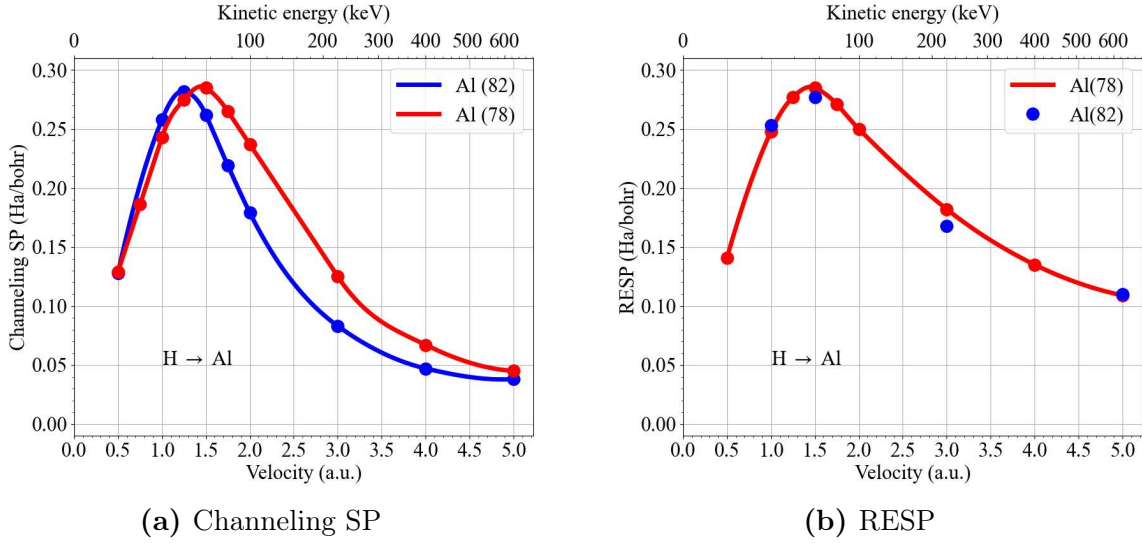


**Figure 6.3.1:** Center shifting of the fcc aluminum cluster oriented at  $[001]$ . The atom-centered aluminum cluster with 82 atoms is named as Al(82) and the channel-centered cluster with 78 atoms is named as Al(78). The spheres represent the aluminum atoms projected onto the  $xy$  plane and the axial direction is given at the left corner of the figure. Among these spheres, those with fully opaque coloration are within the cluster limited by the orange circle, while those with more transparent coloration illustrate the potential extension of the cluster. Atoms with the best basis quality is represented by the pink color, the second best with grey color and the least good with green color. The black cross marks the cluster center with the orange triangle being the sampling zone of impact parameters.

There is one modification in the target modeling of the aluminum cluster comparing to that of the lithium cluster. While running the channeling calculations, we have observed that a shift in the cluster center gives us stronger stopping powers at a large range of velocities. Figure 6.3.1 demonstrates how this shift is made in a cluster of fcc aluminum at direction  $[001]$ . Some of our early calculations are conducted in a cluster centered on the central column of atoms. In the case of aluminum, this corresponds to a cluster composed of 82 atoms. When the center is shifted to the channel of the cluster, the radius and the length are both kept unchanged, leading finally to an aluminum cluster of 78 atoms.

In figure 6.3.2 we compare both the channeling SP and the RESP of hydrogen in aluminum centered at the two positions mentioned above. Starting with the channeling condition (left-hand image), the difference between the two curves is small at low velocities

and becomes more remarkable at higher velocities. Centered at the central atoms the cluster Al(82) gives a SP curve that peaks at  $v = 1.25$  a.u. (40 keV), whereas the cluster Al(78) centered at the channel gives a curve that peaks at  $v = 1.5$  a.u. (60 keV). Before  $v = 1.25$  a.u. the results from Al(82) are slightly higher than those from Al(78). Then the two curves cross over and the results of Al(82) become much lower than that of Al(78), with the largest difference between them reaching 50%. As the velocities rises from  $v = 4.0$  a.u. (400 keV) onward, the gap between the two SP curves reduces again.



**Figure 6.3.2:** Stopping powers of hydrogen (DZ) in fcc [001] aluminum (ACQZ/DZ/DZ) with different cluster centers. The image on the left hand shows how the channeling SP is altered by shifting the cluster center and the image on the right hand shows how the RESP is affected by this shift. In both images the results from the atom-centered cluster Al(82) are reported by either a blue line with round markers or only blue markers, and the results from the channel-centered Al(78) are reported by a red line with round markers.

One possible cause to the changes in the channeling SP after shifting the cluster center might be that the projectile passing through the channel of Al(78) is in a more symmetric electron density environment than in the channel of Al(82). As we can see in figure 6.3.1, the channel in Al(82) is quite close to the surface while in Al(78) it sits right in the center of the bulk. In addition, since we apply a mixture of basis quality to the clusters, the channel-centered cluster offers a more homogeneous basis surrounding to the projectile. Of course we can create the same homogeneity in the atom-centered cluster by putting the best basis on outer layers of atoms, but the price to pay is very high. Considering the bulk electron density and the basis quality homogeneity, the channel-centered Al(78) seems the most suitable for the channeling SP calculations. However when the projectile is off-channel inside the impact zone (shown as orange triangles in figure 6.3.1), it might

not feel the surface as much as it does when in the channel and the heterogeneity of the basis surrounding would be averaged out over all the trajectories. This leads us to further investigate the impacts of cluster center shifting on the RESP.

The right-side image of figure 6.3.2 shows how shifting the cluster center influence the RESP. Since multiple trajectories need to be run before obtaining the RESP at a given velocity, the computational cost is expensive for a full-scale velocity study. Therefore certain representative points at  $v = 1.0, 1.5, 3.0$ , and  $5.0$  a.u. are selected for the calculations in Al(82) in order to save machine efforts. Despite of the few data points, it is clear to see that the shift in cluster center does not have a pronounced effect on the RESP values. The largest difference between the results of Al(78) and Al(82) is 8% and their average difference is only 2%.

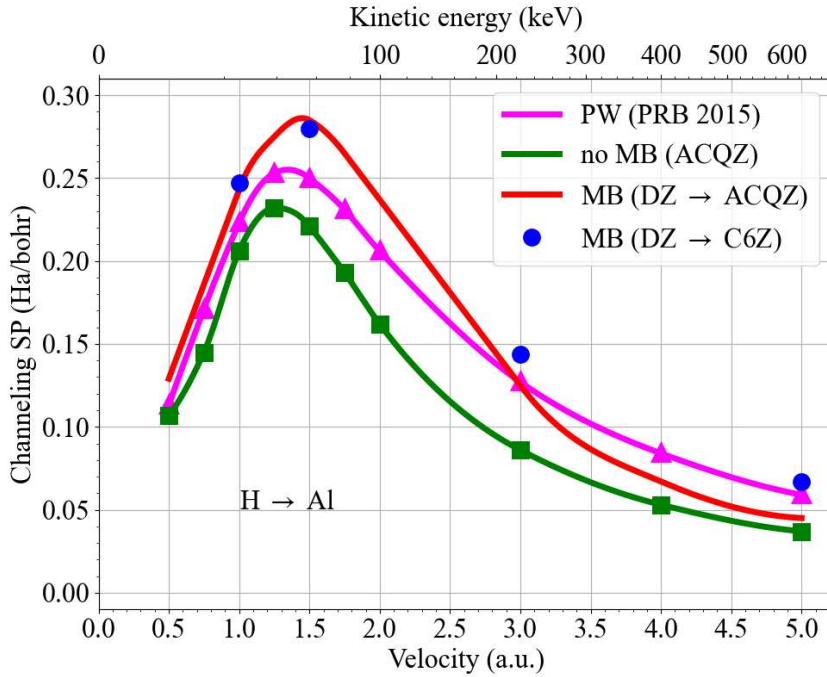
Taking into account of both the more symmetric channeling environment and the barely altered RESP, we have decided to continue our research in aluminum using the channel-centered Al(78) cluster. Besides these two reasons, the 4 less atoms in the Al(78) cluster comparing to the Al(82) cluster make our simulations slightly lighter.

Additionally, we notice in figure 6.3.2 that the channeling SP and RESP are very similar in magnitude before  $v = 2.0$  a.u.. At higher velocities the RESP becomes superior in value and doubles the channeling SP at  $v = 5.0$  a.u.. This observation can be explained by the fact that off-channel trajectories usually give stronger stopping powers than that of the channel. The difference between these two conditions has been studied in many experiments by tilting the surface of single crystal targets normal to that of the incident ion beam direction [114, 115, 116]. While we lack the experimental data for proton and helium in aluminum to quantify the channeling stopping powers presented in this chapter, it would be interesting in the future to benchmark against channeling experiments carried out in other systems.

### 6.3.1 Hydrogen channeling

The first case we talk about is hydrogen in aluminum. Here we compare not only between the absence (no MB) and the presence (MB) of the projectile basis, but also benchmark against the RT-TDDFT calculations of Schleife *et al.* [77] done using the plane-wave (PW) basis. Figure 6.3.3 reports the above-mentioned channeling stopping power for velocities ranging from  $0.5$  (6 keV) to  $5.0$  a.u. (625 keV). Unless mentioned

otherwise, the basis sets used in our simulations are DZ for hydrogen and ACQZ/DZ/DZ for aluminum.



**Figure 6.3.3:** Channeling SP of hydrogen in aluminum at different velocities. Results from the benchmark study using the plane-wave (PW) method [77] is reported by the pink solid line. The green solid line shows results from simulations without projectile basis (no MB) and the red solid line represents for simulations with projectile basis DZ (MB). The target basis in those two cases are ACQZ/DZ/DZ. Blue dots gives the results calculated by using DZ on the projectile and C6Z/DZ/DZ on the target.

Let us begin by comparing the results of no MB to that of PW calculations. Despite of a lower magnitude in the absolute values, the no MB curve follows the same trend as that of the PW curve. Discrepancy between these two sets of results is smaller and varies between 5% and 15% before the peak at  $v = 1.25$  a.u. (40 keV), and gets wider at higher velocities with the largest gap reaching almost 40%.

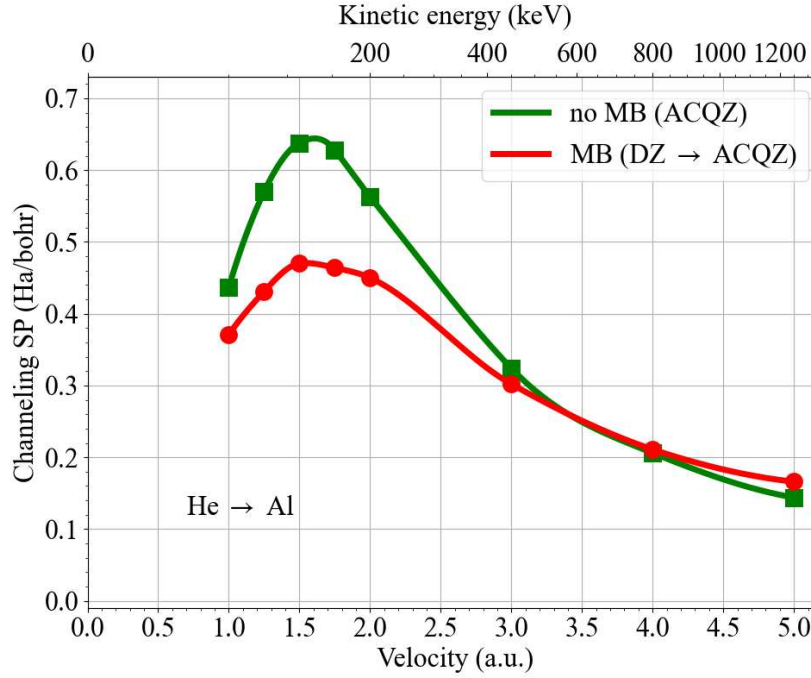
We then look at the results from the MB calculations. Comparing to the PW curve, the MB curve is higher in magnitude until  $v = 3.0$  a.u. (225 keV) before going under for the rest of the velocities. The disagreement between these two methods is within 15% before the crossover and reaches 25% afterwards. Even though the MB curve becomes inferior to the PW curve eventually, it stays above the no MB curve and tends to join the latter at higher velocities. In terms of the general shape, comparing to the other two, the MB curve peaks at a slightly higher velocity and has a steeper drop from the peak before the decrease gets smoother from  $v = 3.0$  a.u. on.

Finally we have added a few results from using the C6Z/DZ/DZ basis mixture on aluminum. It is obvious from the figure that despite of slightly higher absolute values due to a more complete target basis set, especially at high velocities, the global trend of the stopping power stays the same as that obtained with lower quality target basis (CQZ/DZ/DZ). This justifies our choice of a more economic basis set for qualitative analysis.

Regarding the discrepancy among the curves in figure 6.3.3, it is difficult to conclude which one gives better results. Instead, we can observe a general coherence among them in relation to the projectile velocity. Since the channeling condition is only one special case of all the possible trajectories, we will be able to extract more information from the random electron stopping power in a later section.

### 6.3.2 Helium channeling

Another light projectile we study for the channeling SP is helium. The aluminum target used in this case is identical to that of the hydrogen channeling SP analysis presented previously. Because we do not have a second reference to compare with the MB calculations, we will compare between the MB and the no MB results to understand changes brought by the projectile basis. Figure 6.3.4 shows at several velocities the channeling SP obtained with these two basis settings.



**Figure 6.3.4:** Channeling SP of helium in fcc [001] aluminum at different velocities. The green line shows results from simulations without projectile basis (no MB) and the red line represents for simulations with projectile basis DZ (MB). The target basis in those two cases are ACQZ/DZ/DZ.

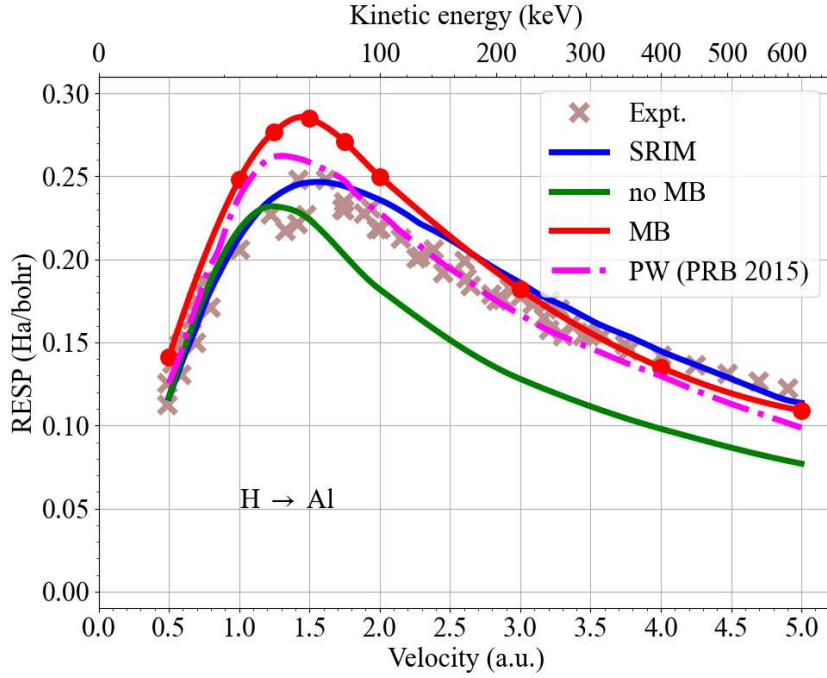
In terms of the general trend, the no MB curve peaks sharply at  $v = 1.5$  a.u. (225 keV) before dropping off while the MB curve presents a much smoother peak at the same velocity and has a more gradual descend at higher velocities. Looking at the absolute values we see that, unlike the case with hydrogen projectile where the MB results exceed the no MB results at all velocities studied, here the MB curve is far below the no MB curve before crossing over at  $v = 3.5$  a.u. (1.2 MeV). After this point, with different declining rates, the two curves slightly diverge. The largest discrepancy in SP between these two basis settings reaches almost 30% around the peaks. However large this disagreement is, we cannot learn more from this internal comparison where the calculation method is the same (remember the only difference between these two sets of values is the presence or absence of the projectile basis). We will therefore move on to the RESP where we can benchmark against the experimental data and the calculations done with other methods.

## 6.4 Random Electronic Stopping Power in Aluminum

In this section we will discuss about the random electronic stopping power (RESP) of three projectiles in aluminum. The first two, hydrogen and helium, are light projectiles without core electrons. The third one, aluminum, is a heavier projectile with 10 core electrons in the  $1s2s2p$  shells and 3 valence electrons in the  $3s3p$  shells. The target aluminum used is identical to that of the channeling calculations, which is a 78-atom fcc cluster of [001] direction with a length of 24.3 Å and a diameter of 6.4 Å centered at the channel. The only difference in the simulation setups of these three projectile studies is the basis quality. For the two light projectiles, we have applied the ACQZ/DZ/DZ mixture on the target. For the aluminum projectile, based on the conclusions drawn from the target basis convergence test (see figure 6.1.4) we have decided to use the less expensive CQZ/DZ/DZ mixture to compare with the most complete C6Z/DZ/DZ basis mixture. For all of these three projectiles, we have run calculations with the DZ projectile basis. Finally with the aluminum projectile, supplementary sets of calculations using the CDZ projectile basis are carried out according to the decisions made from the projectile basis convergence test in figure 6.1.6.

### 6.4.1 Hydrogen in aluminum

Let us start with the hydrogen projectile. Figure 6.4.1 reports many sets of results for the RESP of hydrogen in aluminum from  $v = 0.5$  a.u. (6 keV) until  $v = 5.0$  a.u. (625 keV). Apart from our MOLGW localized GTO basis simulations calculated both with (MB) and without (no MB) projectile basis, we also cite some experimental data [117, 118, 119, 120], the SRIM prediction from the online database [18], and results from the plane-wave (PW) basis calculations of Schleife *et al.* [77]. In fact, the experimental data are so abundant in the SRIM database for this system that we have selected only four sources to avoid a messy figure. It is clear that in this case the SRIM prediction is well supported by the experiments which makes the former a reliable reference.



**Figure 6.4.1:** RESP of hydrogen in fcc [001] aluminum as a function of velocity. The experimental data [117, 118, 119, 120] are marked by the brown crosses and the SRIM prediction [18] is given by the blue solid line. The results from our calculations using DZ as projectile basis (MB) and ACQZ/DZ/DZ as target basis are represented by the red solid line with round markers. The no MB results calculated under the same parameters are plotted by the green solid line. Finally the pink dotted broken line represents the results from Schleife *et al.* [77] using the plane-wave (PW) basis.

First we compare the no MB results to the SRIM prediction. At low velocities, the no MB curve is almost in superposition with the SRIM curve. These two curves separate when the former peaks at  $v = 1.25$  a.u. (40 keV) and the latter peaks at  $v = 1.5$  a.u. (60 keV). The no MB results then drop significantly after the peak and continue to underestimate the SRIM prediction as the velocity increases. At their largest difference, the no MB curve is 50% away from the SRIM curve.

The MB results on the other hand overestimate the SRIM prediction up to 20% before the crossing point at  $v = 2.5$  a.u. (160 keV). Then the MB curve goes slightly under the SRIM curve until approaching the latter again at  $v = 5.0$  a.u.. At the same time the peak positions of these two curves are identical at  $v = 1.5$  a.u.. When compared to the no MB results, the values of the MB curve are higher at the entire velocity range studied and the peak velocity of the latter is slight higher than that of the former. This relationship between the MB and the no MB curves is consistent with that observed for the channeling SP in figure 6.3.3. What is different from the channeling case is that instead of closing the

gap with the no MB curve at higher velocities, the MB curve in the RESP case keeps an almost constant distance with the no MB curve.

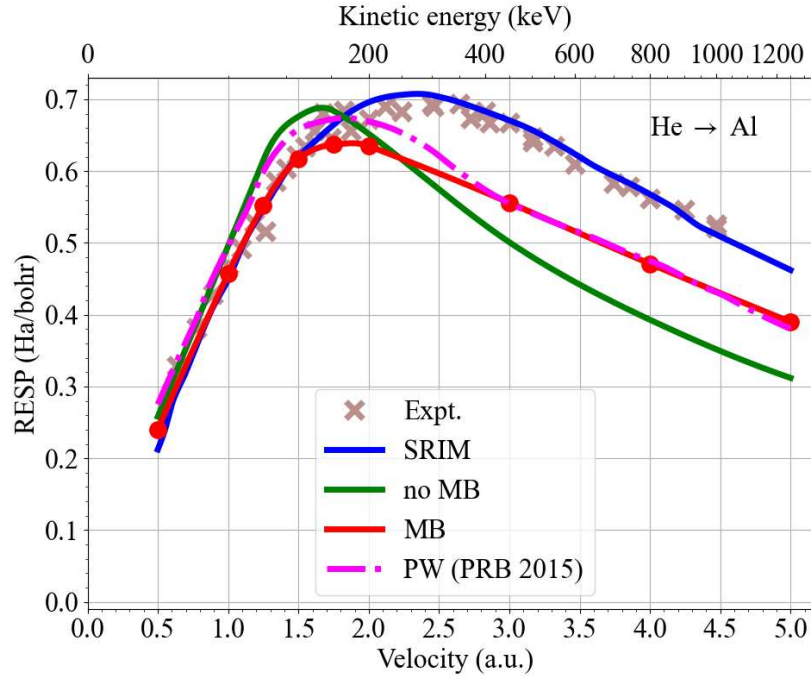
At last we compare our MOLGW results to the PW study. The no MB curve resembles a lot the PW curve in shape and these two share the same peak position. While the MB curve has its peak at a slightly higher velocity, its shape is not significantly different from that of the PW curve. In terms of the magnitude, despite of similar values before  $v = 1.0$  a.u., the no MB results are much lower than the PW results after this point. The agreement is much better between the MB results and the PW results. Outside the peak area, values given by the MB calculations are only slightly higher than that of the PW calculations. Around the peak, the difference between these two sets of results becomes more important and reaches up to 13%. The relationship between the no MB, the MB and the PW curves is similar to that observed for the channeling SP in figure 6.3.3, except that the MB results stay above the PW results in the case of RESP instead of crossing it over. At the same time when benchmarking the PW curve against the SRIM prediction and the experiments there is a general good agreement. The PW results overestimate the latter two to some small degree around  $v = 1.25$  a.u. and start to underestimate them after  $v = 4.0$  a.u..

To conclude on the RESP of hydrogen in aluminum, we see that the general trend of the MB results is correct comparing to the SRIM prediction and the experiments. They have peaks at the same velocity and good agreements in values after  $v = 2.5$  a.u.. It is also encouraging that the PW calculations give similar results to that of our MB calculations, which adds more validity to our approach. When comparing the MB to the no MB results, we notice a remarkable improvement of the peak position and of the RESP values at  $v \geq 1.0$  a.u. by adding the moving projectile basis. Finally, the similarity between the channeling SP and the RESP proves the qualitative nature of the channeling analysis while their differences emphasize the importance of considering random trajectories.

## 6.4.2 Helium in aluminum

Now we look at the RESP of helium in aluminum. In figure 6.4.2 we quote some experimental data [121, 122, 123] cited by the online SRIM database followed by the SRIM prediction [18]. Like in the case of hydrogen in aluminum, there are numerous experiments that support the SRIM prediction so only three sets of experimental data are displayed here. At the same time the good coherence with the experiments makes SRIM a reliable

reference. Apart from findings of our MOLGW localized GTO basis calculations with (MB) and without (no MB) projectile basis, we also show in figure 6.4.2 results from the plans-wave (PW) basis simulations carried out by Schleife *et al.* [77].



**Figure 6.4.2:** RESP of helium in fcc [001] aluminum as a function of velocity. The experimental data [121, 122, 123] are marked by the brown crosses and the SRIM prediction [18] is given by the blue solid line. The results from our calculations using DZ as projectile basis (MB) and ACQZ/DZ/DZ as target basis are represented by the red solid line with round markers. The no MB results calculated under the same parameters are plotted by the green solid line. Finally the pink dotted broken line represents the results from Schleife *et al.* [77] using the plane-wave (PW) basis.

Starting from the no MB results, we see that at low velocities before the peak at  $v = 1.75$  a.u. (310 keV), the no MB curve is very close to the SRIM prediction. The peak of the SRIM curve on the other hand is near  $v = 2.25$  a.u. (510 keV). These two curves cross over soon after the no MB peak and from then on the distance between them stays vast. The largest underestimation of the SRIM results by the no MB calculations reaches almost 50%.

Moving on to the MB results, we notice that the shape of the MB curve is quite similar to that of the SRIM curve. These two sets of values are nearly identical until  $v = 1.5$  a.u. (225 keV) where the MB curve separates away and starts to underestimate the SRIM curve. It is worth noticing that the biggest difference between the MB and the SRIM curves is 20% which is less than half of the largest discrepancy between the no MB and the SRIM

curves. The peak of the MB curve is at the same velocity as that of the no MB curve, before which the former has lower values than the latter. The cross-over between these two happens at  $v = 2.25$  a.u. and the MB results stay above the no MB results afterwards. The relationship between the MB and no MB RESP curves are partially in line with that of the channeling SP in figure 6.3.4 except that the peak positions of these two curves are slightly different and their cross-over happens much later in the channeling case. The disagreement between the two basis settings at high velocities is also much more pronounced in RESP than under the channeling condition.

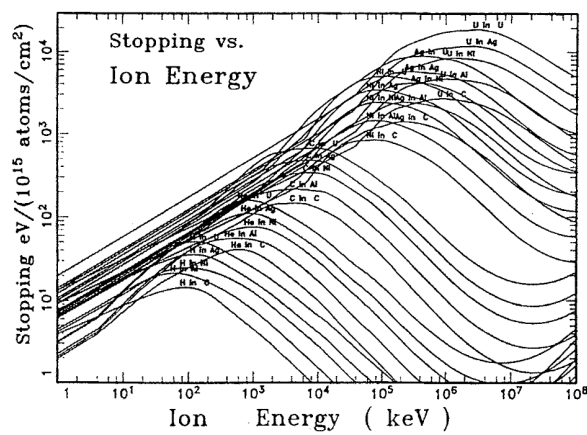
Finally we compare our MOLGW results with that of the PW method. The PW curve has the same peak position as that of both the MB and no MB curves and its shape resembles a lot that of the MB curve. At low velocities before the peak, the PW results are almost identical to that of the no MB calculations and slightly higher than that of the MB calculations. Right after the peak the PW curve becomes higher in magnitude than the no MB curve and continues to be above the MB curve until  $v = 3.0$  a.u. (900 keV). After this point the PW and the MB curves are joint together until signs of separation at  $v = 5.0$  a.u. (2.5 MeV). When compared with the SRIM prediction, the PW results are in good agreement with the former before the peak at  $v = 1.75$  a.u. and then drop to underestimate it at higher velocities. This behavior is very similar both in trend and values to that of the MB curve.

Summarizing from all the comparisons done above, we see that for the RESP of helium in aluminum, the MB calculations give very good results at low velocities. Although they underestimate the experimental data at velocities beyond  $v = 1.5$  a.u., they are in strong agreement with the PW simulations which is a significant improvement over the no MB calculations. Comparing to the channeling SP where we have observed the MB results to be smaller than the no MB results until  $v = 4.0$  a.u., the inclusion of random trajectories have shown us a much earlier cross-over and greater discrepancy at high velocities. Judging from the good performance of the MB calculations for both the hydrogen and the helium stopping powers, we have gained the confidence to proceed with a heavier projectile in aluminum.

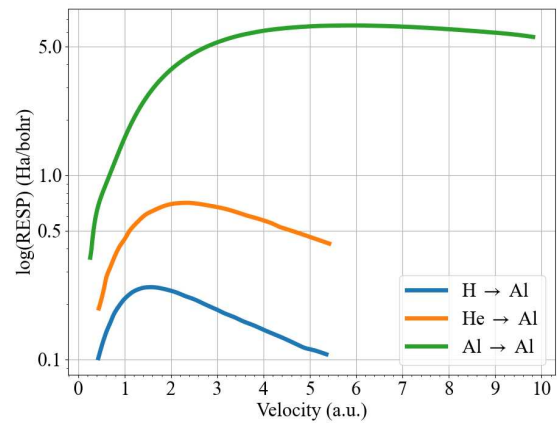
### 6.4.3 Aluminum in aluminum

Having studied extensively the stopping power of two light projectiles (hydrogen and helium) in both lithium and aluminum and obtained relatively good results, we have decided to move on to a heavier projectile. Aluminum stands out as an ideal candidate since it has core electrons in the  $s$  and  $p$  shells but does not possess occupied  $d$  orbitals. This is thus a relatively light but reasonably complex electron configuration for the projectile. At the same time we have chosen to continue working with aluminum as the target for the same reason, with additional argument being that the stopping power experiments within this material are well documented in the SRIM database [18]. The geometry parameters used in this study are the same as in the case of light projectiles, although we do not rule out the possibility that the convergence trend might be different with a heavier projectile. This should be verified by further investigations.

The range of projectile velocities studied is carefully chosen. As demonstrated by the stopping powers of different ions in various solid targets in figure 6.4.3, cited from the historical review of reference [19], we observe a general trend where heavier projectiles have their stopping power maximums at higher kinetic energies. Focusing on this behavior in the aluminum target, we have plotted the SRIM-predicted stopping power in figure 6.4.4 for the three projectiles studied: hydrogen, helium and aluminum.



**Figure 6.4.3:** Cited image of stopping powers of ions (from H to U) in various solids (from C to U) from the historical review of reference [19].

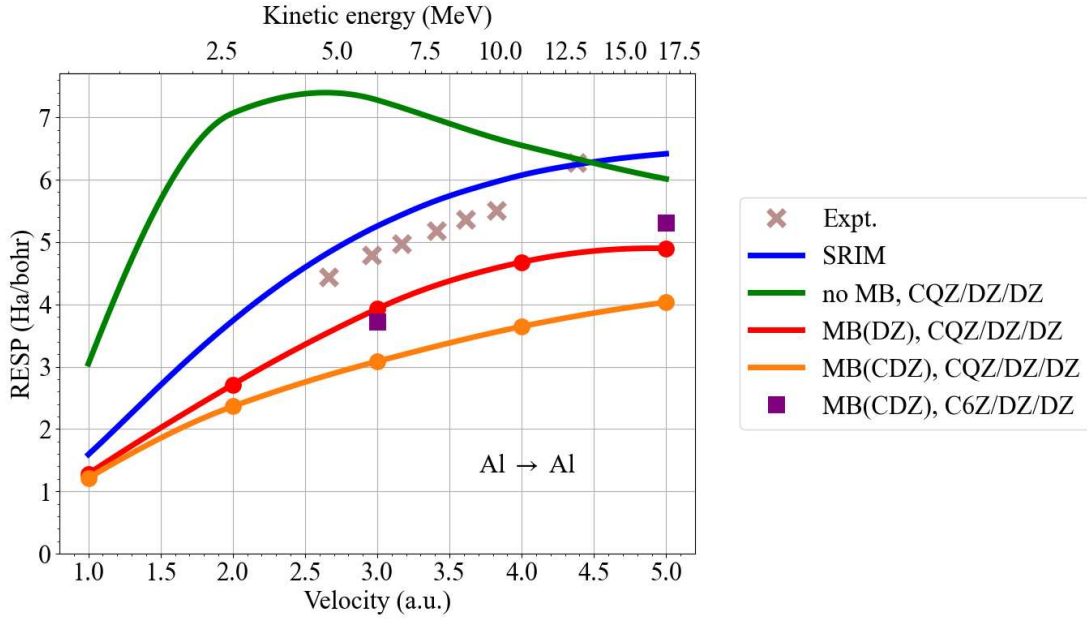


**Figure 6.4.4:** RESP of various ions in aluminum target from the SRIM online database [18] (hydrogen and helium projectile) and the SRIM software (aluminum projectile). The values are reported in logscale.

We notice in figure 6.4.4 that the magnitude of the RESP increases significantly as the projectile becomes heavier. The maximum of aluminum RESP is about 25 times that of the hydrogen RESP and 10 times that of the helium RESP. Looking at the peak positions of these three projectiles, it is obvious that the heavier the projectile, the higher the peak velocity. While hydrogen and helium SP reach their maximum at  $v = 1.5$  and  $2.25$  a.u., the aluminum SP peaks at  $v = 6.0$  a.u.. This is not favourable for our MB calculations as we have seen in the left-hand image of figure 4.1.1, the precision of equation (4.1.55) is quickly compromised at large velocities which requires enormous basis sets to overcome. Constrained by time and resources, we will thus concentrate our efforts on the relatively low projectile velocities  $v \leq 5.0$  a.u. in the study of aluminum in aluminum.

Based on the basis set convergence tests shown in figure 6.1.4 and 6.1.6, we have chosen the lighter CQZ/DZ/DZ mixture in this study rather than the ACQZ/DZ/DZ mixture used in the light projectiles cases. Ideally we should use C6Z/DZ/DZ for better convergence, but the computational burden limits us to perform calculations with this basis mixture only at a couple of velocities to compare with the CQZ/DZ/DZ mixture. For the projectile, simulations with both the DZ and CDZ basis are conducted, taking into account of the conclusions from figure 6.1.6 that the CXZ basis give more converged results than the standard XZ basis.

In figure 6.4.5 we demonstrate the results of the random electronic stopping power (RESP) of aluminum in aluminum obtained using MOLGW both with (MB) and without (no MB) projectile basis. Some experimental data [80, 81] as well as the SRIM prediction are cited for comparison. We would like to point out that the SRIM results in this case is not cited directly from the online database [18] but rather calculated using the SRIM software.



**Figure 6.4.5:** RESP of aluminum in fcc [001] aluminum as a function of velocity. The experimental data [80, 81] are marked by the brown crosses and the SRIM prediction [18] is given by the blue line. The no MB results calculated using the CQZ/DZ/DZ target basis are plotted by the green line. The MB results using DZ projectile basis and CQZ/DZ/DZ target basis are represented by the red line with round markers, and the results using CDZ projectile basis are plotted with the orange line with round markers. Finally purple squares are used to mark results obtained with C6Z/DZ/DZ target basis and CDZ projectile basis.

Looking at the experimental data we notice that the experiments are scarce at projectile velocities lower than 5.0 a.u. (17 MeV). The single data point passed by the SRIM curve comes from a series of data [80] obtained at higher velocities outside the scope of this study. The remaining experimental data [81] are all overestimated by the SRIM prediction by almost 10% and the peak of SRIM is evidently beyond  $v = 5.0$  a.u.

We will now bring our attention to the no MB results. This setup cannot represent the initial neutral charge state of the projectile since without the projectile basis all electrons from the projectile are considered as target electrons. Consequently if we consider a neutral aluminum atom as projectile in the MB calculations, we would get a fully-stripped aluminum ion travelling in a negatively charged aluminum target in the no MB simulations. It would make more sense to calculate the no MB scenario using an initially fully-stripped projectile, but we would still be in short of the corresponding MB results for comparison as the MB simulations cannot produce a striped ion. Admitting that it would not be meaningful to compare in depth the no MB results with the others, we will simply look at the apparent differences between them. While the no MB curve passes through one experimental point

little before  $v = 4.5$  a.u. (14 MeV), it has largely missed all others. When comparing it to the SRIM prediction, we see two distinctive shapes and that the no MB curve peaks at a much lower velocity  $v = 2.5$  a.u. (4.2 MeV).

Let us move on to the MB calculations. Three sets of results are reported here. Two of them use the CQZ/DZ/DZ mixture on target atoms with different projectile basis: DZ and CDZ. The third one keeps the CDZ projectile basis and increases the target basis quality to C6Z/DZ/DZ. We will start comparing between the two different projectile basis with the CQZ/DZ/DZ target basis. When using DZ on the projectile, the shape of the MB curve resembles a lot that of the SRIM curve. Comparing to the experimental data, the values from the DZ projectile basis simulations underestimate the former by roughly 20%. On the other hand with the CDZ projectile basis, the MB curve is flatter and underestimates even more the experimental data (almost 40% lower than the experiments). The difference between the DZ and CDZ simulations is consistent with the projectile basis convergence test shown in figure 6.1.6.

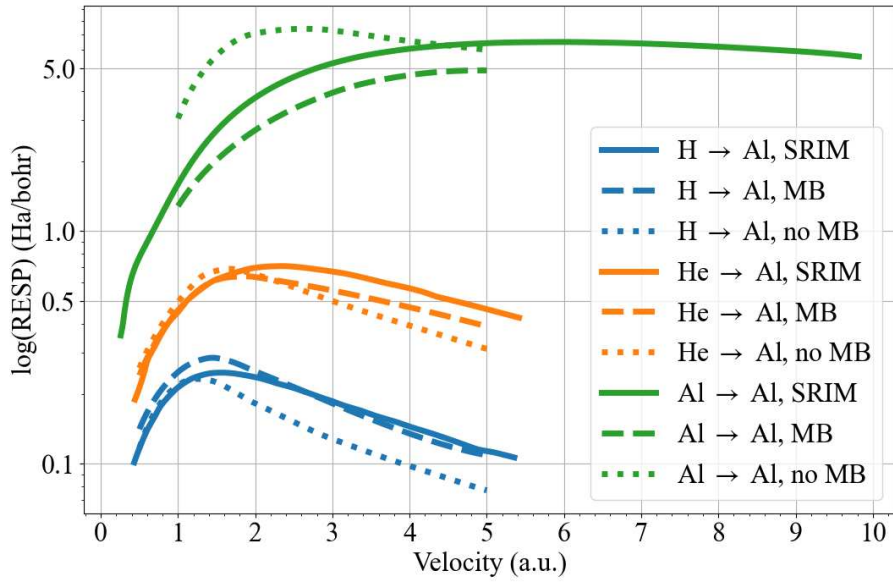
Having observed from the convergence test that raising the cardinal number  $X$  of the CXZ basis on the projectile does not necessarily improve the stopping powers, we would like to see if any progress can be made by using the more complete C6Z/DZ/DZ target basis. Due to the huge computational efforts entailed, results are given at only two velocities  $v = 3.0$  and  $5.0$  a.u.. Significant improvements of 20% and 30% are observed at these velocities comparing to the results obtained with CQZ/DZ/DZ target and CDZ projectile basis. This is consistent with the target basis convergence and emphasises the need of better target basis. At the same time results from the CDZ + C6Z/DZ/DZ combination are very similar to those obtained with the DZ + CQZ/DZ/DZ combination. Whether the latter with low quality basis is truly reliable to replace the more expensive basis combination is still open to discussion.

In this section we have reviewed some firsthand RESP results of aluminum in aluminum. There are only a few experimental data to refer to in the range of velocities that we have studied, thus the SRIM prediction is not well supported. The no MB calculations can only represent an extreme situation where the projectile is fully striped and produce results in striking disagreement with the experiments. Our MB calculations, though underestimate the experimental data by a non-negligible degree, improve largely the no MB results and produce curves that correctly follow the evolution of the experimental data.

There are a few directions that we can take in order to further improve our MB results. First we have to double check the geometry convergence. The conclusions drawn from the figures 6.1.2 and 6.1.3 are based on a very light projectile hydrogen and might no longer be valid for the aluminum projectile. Then we can raise the basis quality on both the target and the projectile. The CXZ basis sets with high cardinal numbers are a promising place to start, yet there might be better basis to be tested. Once the precision at low velocities is improved, it would be interesting to explore higher velocities near the RESP peak where the SRIM prediction is in better agreement with the experimental data.

Meanwhile when experiments in a system are not numerous enough to support the SRIM prediction, it is not wise to consider the latter as the standard answer and one can expect the *ab initio* results to differ from the SRIM calculations. Take the study of Ullah *et al.* [78] for example, where the stopping power of nickel in nickel is calculated with the plane-wave (PW) basis using the QB@LL program [62, 63]. Despite of the existence of a SRIM prediction, there is no experimental data cited by the online SRIM database [18] for the velocity range studied. While the work of Ullah shows excellent improvement of results aided by the inclusion of both target and projectile core electrons, it still differs from the SRIM curve by at least 15%. Therefore even if we improve our results for aluminum in aluminum, we might still be in relatively large discrepancy with the SRIM prediction which is not fully backed by experiments.

Finally, to highlight the important contributions from the moving projectiles basis, we compare in figure 6.4.6 the RESP of SRIM, MB and no MB calculations for the three projectiles studied in aluminum. First we comment that the form of the MB curves are always in good agreement with that of the SRIM prediction and better than that of the no MB curves. This is especially true for aluminum in aluminum. In the second place, we remark that the RESP values given by the MB calculations are much closer to the SRIM data than the no MB calculations have achieved, especially at higher velocities. At last, we notice that the peak positions of the MB curves are also more accurate than those of the no MB curves. Those three points of improvement strongly suggest that the MB calculations are a necessary upgrade of the no MB calculations in order to capture more accurately the stopping power behaviors.



**Figure 6.4.6:** RESP in logscale of three different projectiles in aluminum: hydrogen (reported with color blue), helium (orange) and aluminum (green). Predictions from SRIM [18] are plotted with solid lines. Results calculated with projectile basis (MB) are plotted with broken lines and results obtained without projectile basis (no MB) are given with dotted lines.

# Chapter 7

## Conclusion

The current global climate crisis makes an urgent call to reduce greenhouse gases emissions and replace fossil fuels by alternative energy sources like the nuclear power. With a history of destructive accidents, the safety of nuclear reactors is undeniably an important research topic. Experimental studies traditionally use neutron beams to irradiate materials and reproduce nuclear damages. These installations are not only expensive but also difficult to operate. In recent years, ion beam irradiation become a popular alternative to emulate neutron-induced damages thanks to its lower costs and less harmful exposures. The JANNuS [16, 17] laboratory in CEA Saclay possesses a powerful ion beam facility with three ion accelerators and is capable of implanting a large variety of ions inside multiple types of materials.

The experimental measurements of ion irradiation, such as the electronic stopping powers, are commonly benchmarked against the empirical predictions from the software SRIM [18, 19]. The results from SRIM give excellent accuracy for systems whose records of experimental data are rich, but become much less reliable when such data are scarce. Calculations from first-principles like ours provide therefore supplementary references to experimental studies. Implemented inside MOLGW [47], we combine the stationary DFT and the real-time TDDFT to simulate the electronic stopping powers of ions in matter using localized GTO basis. Comparing to the plane-wave basis used in Qbox/Qb@ll [62, 63] and Octopus [124], the localized basis is advantageous in describing all electrons (core and valence) and storing information in matrix forms. Although programs like SIESTA [66] and CP2K [67] also use localized basis to solve the RT-TDDFT problems, our development in MOLGW stands out with the addition of moving projectile basis.

In this conclusive chapter, we will summarize some of the major milestones of this PhD research and discuss about a few ideas that have the potential to further improve the performance of our code and the confidence over our results.

## 7.1 Achievements

After a brief introduction of our research background and the concept of electronic stopping power, we have reviewed in Chapter 2 some fundamental theories about the DFT and the TDDFT and have discussed about several numerical techniques concerning the application of localized GTO basis: the mixture of basis quality, the matrix representations of key physical terms and the approximations used to evaluate the 4-center Hartree potential integrals. For systems without projectile basis, we have simplified the matrix expressions in an orthogonal basis and seen that the MAG2 propagator is more reliable than the CN propagator. Then we have distinguished the single-trajectory stopping power from the random electronic stopping power and proposed a new angled sampling strategy of the impact parameters based on the polar symmetry sampling of Maliyov and coworkers [48].

We have reported in Chapter 3 the stopping powers of proton and antiproton in LiF calculated without projectile basis [46]. Good agreements are achieved between our calculations and the experimental data. Not only have we correctly described the velocity threshold for the proton stopping power and the positive Barkas effect, but also we have observed some unusual behaviors of the antiproton RESP and a negative Barkas effect at very low velocities that is unrecorded in the literature. A plausible cause of the negative Barkas effect is found after the fractional charge and isolated ion analysis. We conclude that the presence of antiproton destabilizes the  $2p$  orbitals of  $F^-$  ion, which lowers the excitation energy of the ion and eventually brings the RESP of antiproton higher than that of proton in LiF at low velocities.

In Chapter 4 we have demonstrated the necessary modifications to the time-dependent equations due to the addition of projectile basis and have studied the extra operator  $\hat{D}$  that describes the projectile basis movement. Some special properties of this operator are presented, including its asymmetric matrix shape, its role in conserving the wave-function orthonormality and its energy contribution  $E_{-iD}$ . We have shown both the analytical and numerical evaluations of  $E_{-iD}$  and have concluded that the numerical precision depends

imperatively on the completeness of the basis set and is more affected at large projectile velocity. At the end of the chapter, the reliability of two major propagators used in MOLGW are weighted up in the absence and presence of projectile basis. The MAG2 propagator, while having better performances in cases without projectile basis, becomes less accurate than the CN propagator due to extra approximations in cases where the projectile basis is present.

The first part of Chapter 5 focuses on the implementation of our theoretical development in MOLGW and on the optimization of the code efficiency. The addition of projectile basis requires the correct updates of the moving basis centers and the modification of the propagation scheme to take into account of the operator  $\hat{D}$ . In order to reduce the computational costs of the step-by-step real-time updates of large matrices, we have selected only the mixed target-projectile elements to be recalculated. The second part of the chapter demonstrates how we validate our implementations with three functionality tests in simple diatomic systems. We have first assured that the ghost sites (basis without atomic cores) alter neither the total energy nor the total electron number. Then we have seen that despite of some small discrepancy, the energy variations are almost identical in the absence and the presence of projectile basis. At last we have switched the roles between the target and the projectile to ensure that the energy variation of the system stays the same. Passing all three tests has given us enough confidence over the healthy performance of our numerical development.

At the beginning of Chapter 6 we have carefully studied the two main groups of modeling parameters vital to the energy stabilization and the convergence of the stopping power in solid targets. We have concluded on the use of long but thin clusters, higher quality CXZ basis on the target, DZ basis for light projectiles and CDZ basis for projectiles with core electrons. Channeling stopping powers of hydrogen and helium are studied in fcc [001] aluminum target and are observed to be sensitive to the centering of the cluster. Considering the electron density symmetry and the homogeneity of target basis quality felt by the projectile, it is preferable to center the aluminum cluster on its channel rather than on its central column of atoms.

The main part of Chapter 6 exhibits random electronic stopping powers from our MOLGW simulations using projectile basis. Although admittedly not fully converged, these results provide accurate qualitative insights. For hydrogen in lithium and aluminum, our

calculations are in good general agreements with the SRIM prediction and the experimental data, as well as with other calculation methods like the linear-response TDDFT [44] and the plane-wave basis real-time TDDFT [77]. For helium in lithium, we lack the experimental data to draw definitive conclusions. As for helium in aluminum, our calculations agree with the SRIM prediction and the experimental data at low velocities and are almost identical to results from the plane-wave basis method [77] at higher velocities. Finally, we report our firsthand results for aluminum in aluminum. Although underestimating the experiments and the SRIM calculations, our results obtained with the projectile basis correctly capture the behaviors of the former two. In almost all cases, the addition of projectile basis brings visible improvements on calculations done without projectile basis.

## 7.2 Perspectives

Despite all the achievements summarized above, there are several aspects of this work that could be improved or further investigated. In Chapter 2 we have proved analytically the expression (4.1.46) of  $E_{-iD}$  for a system where all particles are considered moving. We would like to obtain the same expression for systems with only one moving particle to further support our numerical observations.

In Chapter 4 we have explained how to achieve the change of reference frame by iterating through the SCF cycles with the effective Hamiltonian  $M = H - iD$ . However, this technique currently only works for systems with atomic targets. For solid systems we have to let the projectile propagate a certain distance to reach the steady state. If we could overcome the convergence difficulty of the wave-function re-initialization in solid targets, we might be able to use a shorter cluster.

Significant computational efforts are saved by the optimization techniques presented in Chapter 5. While we have applied the selective recalculations on most of the matrix terms, the  $V_{xc}$  matrix is still fully updated at each time step and can certainly be optimized. In the same chapter, we have observed an  $\Delta E$  anomaly during the ghosts test for helium in real proton target at  $v = 0.5$  a.u. and  $p = 3.0$  bohr. While this is consistent with the Löwdin charge profile of the system, it might be interesting to investigate deeper into the origin of this anomaly.

During the convergence tests in Chapter 6, we have been limited by computer resources

and human time to examine the effects of higher order  $XZ$  and  $CXZ$  basis on the projectile. Continuing efforts on the projectile basis test could give us a clearer picture of the convergence trend. Conclusions on the geometry convergence might also be different when heavier projectiles are used. Additionally, the crystal orientation and the number of impact parameters sampled for the RESP are two other convergence topics that worth re-investigation with moving projectile basis.

While most of our RESP calculations with projectile basis have produced satisfying results in solids, we have observed very unusual results for helium in lithium which requires more experimental data for better understanding. Other systems that lack experimental validation are hydrogen in lithium and aluminum in aluminum at low velocities. In the hope of improving convergence and minimizing discrepancy with reference data, we would need to run simulations with better target and projectile basis, notably in the  $CXZ$  basis group. Longer cluster might also be necessary for better convergence. Apart from these suggested RESP studies, it would be equally interesting to investigate more on the channeling condition of other systems like boron in silicon [115] and nitrogen in silicon [114] by benchmarking MB results against the experimental findings.



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