

Siesta: A Complete Guide

Hand-on 1: Introduction to DFT and Pseudopotentials

Dr. Carlos Maciel de Oliveira Bastos
Postdoctoral Research Fellow

University of Brasilia

24/10/2024





Educational History:

- Undergraduate : *Bachelor of Physics – Federal University of São Carlos (UFSCar) - 2012*
- Master of Science (Physics): *São Carlos Institute of Physics / University of São Paulo (IFSC/USP) - 2015*
- PhD in Physics: *São Carlos Institute of Physics / University of São Paulo (IFSC/USP) - 2019*



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My research focused on condensed matter physics, included:

- effective methods like k·p theory
- ab initio methods, particularly DFT
- III-V semiconductors
- Transition Metal Dichalcogenides (TMDs)
- Low-dimensional structures such as nanowires and superlattices



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Other projects:

- Brewmaster (PronaTec) - 2018
- Commerce Technician (ETEC-CPS) - 2021
- Founder – Fat Cat Brewery (2020)

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About me

Google Acadêmico



Carlos Maciel de Oliveira Bastos

A SEGUIR

International Center of Physics, Institute of Physics, University of Brasilia, 70910-900, Brasilia

Nenhum email confirmado

[Physics](#) [solid state physics](#) [spintronic](#) [nanotechnology](#)

TÍTULO

CITADO POR

ANO

Ab initio investigation of structural stability and exfoliation energies in transition metal dichalcogenides based on Ti-, V-, and Mo-group elements

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2019

CMO Bastos, R Besse, JLF Da Silva, GM Sipahi
Physical Review Materials 3 (4), 044002

Realistic multiband $k \cdot p$ approach from *ab initio* and spin-orbit coupling effects of InAs and InP in wurtzite phase

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PE Farla Junior, T Campos, CMO Bastos, M Gmitra, J Fabian, GM Sipahi
Physical Review B 93 (23), 235204

A comprehensive study of g-factors, elastic, structural and electronic properties of III-V semiconductors using hybrid-density functional theory

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Size-Induced Phase Evolution of MoSe₂ Nanoflakes Revealed by Density Functional Theory

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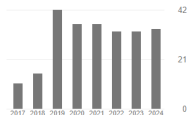
2018

OBTER O MEU PRÓPRIO PERFIL


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VER TUDO

	Todos	Desde 2019
Citações	254	214
Índice h	6	6
Índice i10	6	6



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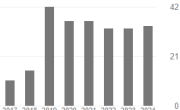
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Ano	Citações
2017	10
2018	15
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2020	35
2021	32
2022	30
2023	30
2024	30

Other research's projects:

- "Desenvolvimento de equipamento medidor de unidades de pasteurização de baixo custo com foco em microcervejarias" - IFSP - Sertãozinho (pedido de patente)
- "Desenvolvimento de metodologia para produção de cerveja sem álcool e estudo da estabilidade microbiológica do produto" - IFSP - Sertãozinho

- 1 What is Siesta?
- 2 A Pedestrian's Guide to Density Functional Theory.
- 3 A Brief history of atomic basis
- 4 A Brief history of pseudopotential
- 5 Create Pseudopotential with ATOM Code

What is Siesta?

The **Spanish Initiative for Electronic Simulations with Thousands of Atoms (SIESTA)**

- It uses the standard Kohn-Sham self-consistent density functional method
- It employs norm-conserving pseudopotentials
- It uses atomic orbitals with finite support as a basis set
- Projects the electron wavefunctions and density onto a real-space grid

What is Siesta?

The **Spanish Initiative for Electronic Simulations with Thousands of Atoms (SIESTA)**

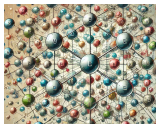
- It uses the standard Kohn-Sham self-consistent density functional method
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SIESTA primarily enables the calculation of:

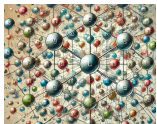
- Total and partial energies.
- Atomic forces.
- Stress tensor.
- Electric dipole moment.
- Electron density.
- Geometry relaxation.
- Spin polarized calculations
- Wannier Functions with Wannier90
- Local and orbital-projected DoS.
- Dielectric polarization.
- Vibrations (phonons).
- Band structure.
- Real-time TDDFT
- Ab-initio Molecular Dynamics
- Transport with TranSIESTA
- Among others

A Pedestrian's Guide to Density Functional Theory

A Pedestrian's Guide to Density Functional Theory.



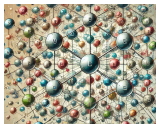
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Many Body Problem

$$H = - \sum_i^N \frac{\hbar^2}{2m} \nabla_{\mathbf{r}_i}^2 - \sum_i^P \frac{\hbar^2}{2M_i} \nabla_{\mathbf{R}_i}^2 + \sum_{i < j}^N \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_i^N \sum_j^P \frac{Z_j e}{|\mathbf{r}_i - \mathbf{R}_j|} + \sum_{i < j}^P \frac{Z_j Z_i}{|\mathbf{R}_i - \mathbf{R}_j|}$$

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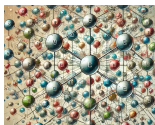
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Born-Oppenheimer Approximation

$$H = H_e + H_n$$

$$H_e = \sum_i^N \frac{\hbar^2}{2m} \nabla_{\mathbf{r}_i}^2 + \sum_{i < j}^N \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_i^N \sum_j^P \frac{Z_j e}{|\mathbf{r}_i - \mathbf{R}_j|}.$$

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Consider the Schrödinger equation for electronic hamiltonian

$$\hat{H}_e |\psi_k\rangle = E_k |\psi_k\rangle \quad (1)$$

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Hohenberg-Kohn Theorems

- In 1964, Pierre Hohenberg and Walter Kohn published two theorems that laid the foundation for modern density functional theory.

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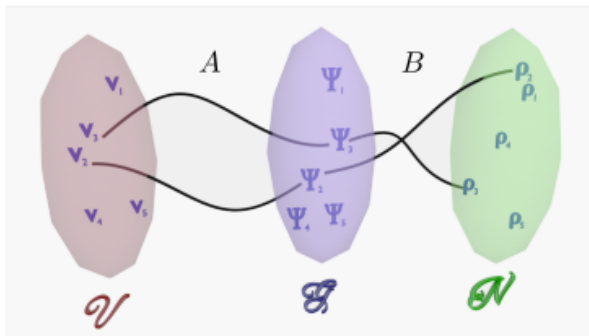
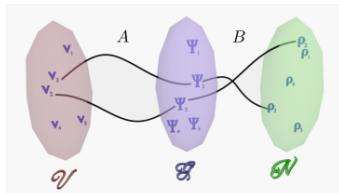


Figure: Mapping between Potential, wavefunction and electronic density

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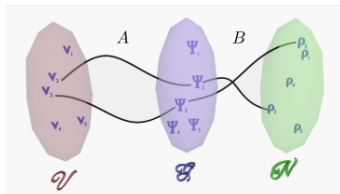
Hohenberg and Kohn showed that the mapping A is unique, meaning it is impossible to obtain the same ground state $|\psi_0\rangle$ from two different external potentials. B mapping is unique too.

First Hohenberg-Konh Theorem

$$|\psi_0\rangle = |\psi[\rho_0]\rangle \quad (2)$$

This theorem is a direct consequence of the correspondence between the V , G and N mapping.

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Second Hohenberg-Konh Theorem

There is also a minimum for $E[\rho]$: if ρ is the ground-state density corresponding to v_{ext} , we have for all densities $\rho' \neq \rho_0$ the following:

$$E[\rho_0] < E[\rho'] \iff E_0 = \min E[\rho], \quad \text{with } \rho \in \mathcal{N}$$

This theorem is a consequence of the variational principle and the unique relationship between ρ and $|\psi_0\rangle$

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Kohn-Sham Formalism

In 1965, Walter Kohn and Lu Sham proposed a method to determine the density for an interacting system using an effective non-interacting system, where the explicit form of the density functional is known.



Electronic Density

- Interacting System
- Real System



Electronic Density

- Non-Interacting System
- Real System



Electronic Density

- Non-Interacting System
- Fictitious system with the electronic density is the same of Real system

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Kohn-Sham Partition Energy

Since the system is non-interacting, the wave function can be constructed using a Slater determinant, using orbitals. The total energy of the system is given by three terms,

$$E[\rho] = T_s[\rho] + E_H[\rho] + E_{xc}[\rho]. \quad (3)$$

Exchange-Correlation Energy

In the Kohn–Sham formalism, the exchange-correlation term $E_{xc}[\rho]$ incorporates the complex many-body effects that are not accounted for by T_s and E_H and requires approximations to be solved.

$$E_{xc}[\rho(r)] = E_x[\rho(r)] + E_c[\rho(r)] + (T[\rho(r)] - T_s[\rho(r)]) + E_{si}[\rho(r)]. \quad (4)$$

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Kohn-Sham equation

the ground state can be obtained using the variational method, which results in the following equation:

$$\{T_s[\rho] + v_H[\rho] + v_{xc}[\rho]\} \phi_i^{\text{KS}}(r) = \epsilon_i \phi_i^{\text{KS}}(r), \quad (5)$$

Kohn-Sham Cycle

This method starts with a trial density $\rho^{(1)}(r)$, allowing the construction of a tentative potential

$$v_s^{(1)}(r) = v_H[\rho^{(1)}](r) + v_{\text{ext}}[\rho^{(1)}](r) + v_{xc}[\rho^{(1)}](r), \quad (6)$$

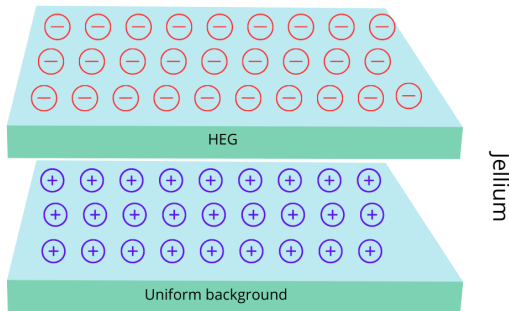
The solution of the equation (5) using the potential $v_s^{(1)}(r)$ then provides a set of orbitals $\phi_i^{\text{KS}(2)}(r)$ that lead to an improved density

$$\rho^{(2)}(r) = \sum_i |\phi_i^{\text{KS}(2)}(r)|^2. \quad (7)$$

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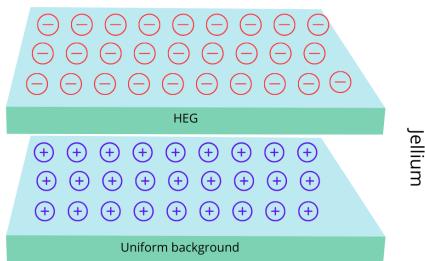
Exchange Correlation Functional

The only term that requires approximation is the exchange-correlation functional and can be analyzed through a model derived from HEG



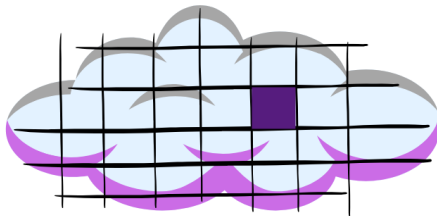
This issue is resolved by incorporating a homogeneous background of positive charge, which cancels the divergence associated with the long-range interaction

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- Using the HEG model, one can derive an approximation for the analytical exchange energy functional.
- Correlation energy functional can be obtained in two distinct regimes: high density and low density.
- In real systems, such as solids and molecules, the electron densities are typically inhomogeneous

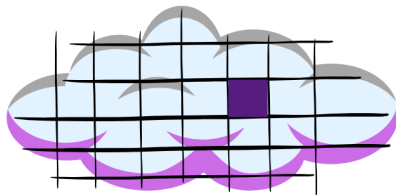
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Local Density Approximation (LDA)

- The inhomogeneous system is treated as if it locally possesses the same density as a HEG, denoted as $\rho_{\text{HGE}} = \rho_{\text{inhom}}$.
- LDA is a first-principles functional of ρ , it does not depend on any free parameters that introduce a physical scale or experimental data, and it is treated locally as an HEG

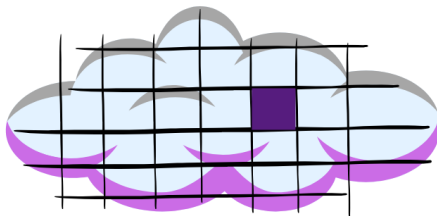
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Generalized Gradient Approximation (GGA)

- GGA incorporates information from both the electron density and its gradient.
- Unlike the LDA, the construction of GGA is not unique, allowing for various parameterizations, PW91 and PBE functionals, among others.
- Both LDA and GGA utilize the HEG framework and share a common deficiency: neither of these approximations can be described a single electron, the exchange term does not simplify to a pure Coulomb self-interaction.

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Hybrid Exchange Correlation functionals

Hybrid functionals combine the exact exchange energy, typically evaluated using the Hartree–Fock (HF) method, with semi-local exchange energy. For example PBE0,

$$E_{XC}^{\text{PBE0}} = E_c^{\text{PBE}} + \alpha E_x^{\text{HF}} + (1 - \alpha) E_x^{\text{PBE}}, \quad (8)$$

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Van der Waals correction

Due to the relatively minor influence of Van der Waals interactions on total energy calculations, their correction is often neglected in the development of most correlation functionals. Van der Waals potentials, expressed as

$$V_{dW} = V_{\text{dip-dip}}(r) + V_{\text{dip-ind}}(r) + V_{\text{London}}(r), \quad (9)$$

- This interaction is part of the Coulomb potential, except London potential.
- London potential describes the interaction between instantaneous dipole moments, which arise from fluctuations in electron distribution

$$V_{\text{London}}(r) = -\frac{3}{2} \frac{\alpha_A \alpha_B}{R_{AB}^6} \frac{I_A I_B}{I_A + I_B}, \quad (10)$$

A brief history of atomic basis

Basis Sets

- A key factor in achieving this scalability is the choice of the basis set.
- A widely used class of basis sets in quantum mechanical calculations is the plane-wave basis set
- In contrast, localized basis sets, such as Gaussian-type orbitals, truncated atomic orbitals, and wavelets, are more efficient in linear-scaling methods.

Numerical Atomic Orbitals (NAOs)

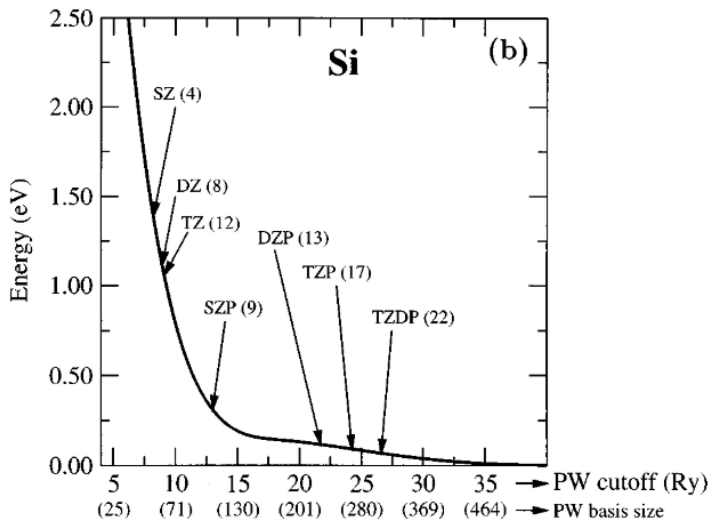
- The initial concept of NAOs stems from the tight-binding approach, focusing on minimal bases (single ζ).
- These atoms are strictly localized, meaning the orbitals become zero beyond a certain cutoff radius r_c
- An extension of this idea is the use of multiple ζ , based on the split-valence concept, but adapted to the strictly localized NAOs.

Single ζ PAO Basis Sets (SZ)

- The starting point is to compute atomic orbitals, using the Kohn-Sham Hamiltonian for isolated pseudoatoms (same exchange-correlation functional and pseudopotential)
- A confining potential is then added to impose boundary conditions on the basis set, truncating the function beyond a certain radius.
- In the minimal basis, SIESTA defines this as Single-Zeta (SZ).

Multiple ζ PAO Basis Sets (DZ,TZ,etc...)

- The first step to increase the flexibility of the basis set is to add a second radial function, resulting in a Double-Zeta (DZ) basis
- This scheme can be extended to include more zetas (Triple-Zeta, etc.)
- Angular flexibility can be introduced by adding shells of higher angular momentum, known as polarization orbitals(P).



Atom	Valence configuration	SZ	DZ	P
		# orbitals symmetry	# orbitals symmetry	# orbitals symmetry
Si	$3s^2 3p^2$	1 s	2 s	1 d_{xy}
		1 p_x	2 p_x	1 d_{yz}
		1 p_y	2 p_y	1 d_{zx}
		1 p_z	2 p_z	1 $d_{x^2-y^2}$
				1 $d_{3z^2-r^2}$
	Total	4	8	(DZ+P) 13

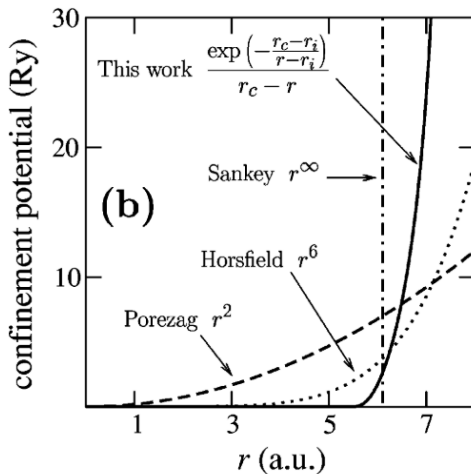
Increase the precision



SZ DZ TZ SZP DZP TZP TZDP



More computational efficient



Cutoff radii parameter

In SIESTA, the cutoff radii are determined based on a single parameter: the energy shift experienced by the orbital when confined, known as the energy shift parameter (PAO.EnergyShift).

A brief history of Pseudopotentials

A brief history of Pseudopotentials

Why Pseudopotential?

- When using atomic basis sets, it is not common to employ pseudopotentials
- pseudopotentials can enhance computational efficiency, especially when core electrons do not significantly contribute to the calculations

A function of the form $e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}$ satisfies Bloch's theorem, which guarantees the preservation of translational symmetry in periodic systems. Using this form as a basis set, the wave function can be expanded as:

$$|\psi_k\rangle = \sum_{\mathbf{G}} C_{k+\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}, \quad (11)$$

A brief history of Pseudopotentials

Therefore, the Schrödinger equation can be expressed as,

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + \hat{V}(\mathbf{r}) \right] \left(\sum_{\mathbf{G}} C_{\mathbf{k}+\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G}) \cdot \mathbf{r}} \right) = \epsilon \left(\sum_{\mathbf{G}} C_{\mathbf{k}+\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G}) \cdot \mathbf{r}} \right). \quad (12)$$

simplify

$$\frac{\hbar^2}{2m} (\mathbf{k} + \mathbf{G})^2 - \epsilon + \int_{V_c} \hat{V}(\mathbf{r}) e^{i(\mathbf{G}+\mathbf{G}') \cdot \mathbf{r}} dV_c = 0, \quad (13)$$

In atomic units, the elements of the Hamiltonian are given by,

$$H_{GG'}(\mathbf{k}) = |\mathbf{k} + \mathbf{G}|^2 \delta_{GG'} + \hat{V}_{G-G'}, \quad (14)$$

with

$$\hat{V}_{G-G'} = \hat{V}_{el}(G - G') + \hat{V}_H(G - G') + \hat{V}_{XC}(G - G'), \quad (15)$$

Depending on the problem, convergence can be slow due to the large number of plane waves necessary to accurately describe the wave function

A brief history of Pseudopotentials

Pseudopotential Method

- In 1940, Herring proposed a method that allows for a reasonable description of the physical properties using a smaller number of plane waves.
- This method introduced the concept of orthogonal plane waves (OPW), which are linear combinations of the core states and plane wave.
- Practically, the OPW functions exhibit plane wave behavior at distances far from atoms but retain atomic characteristics when in proximity to the atomic cores
- In 1959, Phillips and Kleinman, along with Antoncik and Austin, utilized Herring's ideas to simplify the secular equation calculation through a method known as the Pseudopotential Method.

They considered the projection operator for core orbitals,

$$\hat{P} = \sum_c |\phi_c\rangle \langle \phi_c|, \quad (16)$$

A brief history of Pseudopotentials

Pseudopotential Method

An OPW function can then be expressed as,

$$|k + G\rangle_{OPW} = (1 - \hat{P})|k + G\rangle = |k + G\rangle - \sum_c |\phi_c\rangle \langle \phi_c | k + G\rangle. \quad (17)$$

the electronic orbital can be written as a combination of the OPWs,

$$|\phi_{ki}\rangle = (1 - \hat{P}) \sum_G C_{kG} |k + G\rangle. \quad (18)$$

Thus, the Schrödinger equation can be solved using a basis set of the OPWs:

$$\hat{H} |\phi_{ki}\rangle = \epsilon |\phi_{ki}\rangle. \quad (19)$$

A brief history of Pseudopotentials

Pseudopotential Method

Simplifying, we get

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) \right] |k + G\rangle + \sum_c (\epsilon_k - \epsilon_c) |\phi_c\rangle \langle \phi_c| k + G\rangle = \epsilon_k |k + G\rangle \quad (20)$$

Thus, we can write

$$\left[\hat{H} + \sum_c (\epsilon_k - \epsilon_c) |\phi_c\rangle \langle \phi_c| \right] |k + G\rangle = \epsilon_k |k + G\rangle \quad (21)$$

The second term in the equation can be interpreted as a repulsive potential derived from the sum of all core states over the plane wave,

$$\hat{V}_R = \sum_c (\epsilon_k - \epsilon_c) |\phi_c\rangle \langle \phi_c|. \quad (22)$$

A brief history of Pseudopotentials

Pseudopotential Method

Therefore, the states are identical to those of the original Schrödinger equation, independent of the choice of $|\phi_{ki}\rangle$. Thus, we can choose a smooth function, referred to as a pseudofunction. The projector can be written as

$$|\phi_{ki}\rangle = (1 - \hat{P}) |\phi_{ki}^{PS}\rangle, \quad (23)$$

where $|\phi_{ki}^{PS}\rangle$ is called the pseudofunction. The Schrödinger equation can then be expressed as

$$\left[\hat{T} + \hat{V} + \hat{V}_R \right] |\phi_{ki}^{PS}\rangle = \epsilon_k |\phi_{ki}^{PS}\rangle, \quad (24)$$

We can define the pseudopotential as

$$\hat{V}_{PS} = \hat{V} + \hat{V}_R, \quad (25)$$

$$\left[\hat{T} + \hat{V}_{PS} \right] |\phi_{ki}^{PS}\rangle = \epsilon_k |\phi_{ki}^{PS}\rangle. \quad (26)$$

A brief history of Pseudopotentials

Construction of pseudopotential

- It is important to note that this equation is exact, and the eigenstates are the same as those of the original Schrödinger equation.
- they are obtained from a smooth function $|\phi^{PS}\rangle$, which depends on the appropriate choice of the pseudopotential \hat{V}_{PS} , but the pseudopotentials are not unique.
- here are many ways to construct pseudopotentials, which can be divided into two main categories:
 - empirical pseudopotentials, defined from experimental data.
 - ab-initio pseudopotentials, obtained from the solution of the Schrödinger equation for atomic cases.

SIESTA primarily works with norm-conserving pseudopotentials, which is why we will focus on this class.

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A brief history of Pseudopotentials

Norm-conserving pseudopotential

- If we can calculate the norm of the pseudopotential, which is the difference between $|\phi\rangle$ and $|\phi^{PS}\rangle$ the charge in the core regions differs due to variations in the wavefunction in this region.
- This difference in charges in this region represents the norm variation. In the case of norm-conserving pseudopotentials, the core charge must remain the same.

Zunger and Cohen proposed invert the Schrödinger equation for a free ion. Consider the radial part of the free ion equation in atomic units,

$$\left[-\frac{1}{2} \frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} + V_{PS}^l(r) \right] |\psi_{ps,l}\rangle = \epsilon_l |\psi_{ps,l}\rangle. \quad (27)$$

Rearranging this equation yields,

$$V_{PS}^l(r) = \frac{1}{2 |\psi_{ps,l}\rangle} \frac{d^2 |\psi_{ps,l}\rangle}{dr^2} - \frac{l(l+1)}{2r^2} + \epsilon_l \quad (28)$$

A brief history of Pseudopotentials

Norm-conserving pseudopotential

Next, we must find a pseudofunction that matches the wavefunction for distances far from the atomic nucleus, specifically for $r > r_c$, where r_c is the cutoff radius. Thus, we define,

$$|\psi_{ps,l}\rangle = \begin{cases} r^{l+t} f(r) & r < r_c \\ |\psi_l\rangle & r > r_c \end{cases} \quad (29)$$

This can be calculated using DFT by solving the Kohn-Sham equations with an appropriate exchange-correlation functional.

A brief history of Pseudopotentials

Norm-conserving pseudopotential with transferability

In summary, a norm-conserving pseudopotential must possess the following characteristics,

- 1 The eigenvalues obtained for valence states from the pseudopotential must be identical to the original eigenvalues $\epsilon_i^{PS} = \epsilon_i$.
- 2 The all-electron function and the pseudofunction obtained from the pseudopotential must have the same values for $r > r_c$.
- 3 The charge density obtained from 0 to r_c using the pseudopotential must be identical to that obtained from the all-electron solution for $r > r_c$.
- 4 The logarithmic derivative of the pseudofunction must converge to that of the all-electron function for $r > r_c$.

Using the ATOM code

ATOM characteristics

- Perform all-electron DFT atomic calculations for arbitrary electronic configurations.
- Generate ab-initio pseudopotentials.
- Conduct atomic calculations in which the effect of the core is represented by a previously generated pseudopotential.
- Conduct a test to assess the transferability of the generated pseudopotential.

INPUT file

INPUT file

All Electron Calculation

Pseudopotential Generation Using the ATOM Code

Semicore atoms

Transferability Testing of Pseudopotentials Using ATOM

IMPORTANT : TEST YOUR PSEUDOPOTENTIAL