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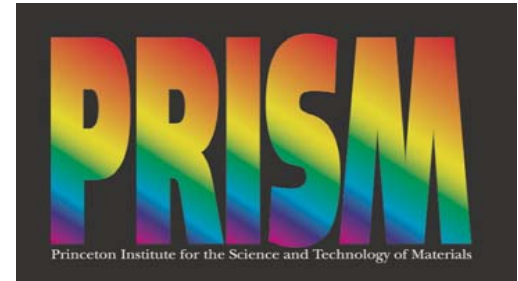
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Introduction to Nanoscale Simulations - Part I

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These are preliminary lecture notes, intended only for distribution to participants.



Electronic Structure Theory: Methods and Applications

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Summary

- Density Functional Theory
- First Principles Molecular Dynamics
- Potential Energy Surfaces and Reaction Pathways
- Coarse Graining in Space and Time

Density Functional Theory

DFT establishes a **new paradigm** for electronic structure calculations:

Use the electron density $\rho(r)$
rather than the wavefunction $\Psi(r_1, r_2, \dots, r_{N_e})$
as basic variable.

This is a great simplification.

If the spatial coordinates are given on a uniform grid with M points, M^{N_e} values are needed to represent $\Psi(r_1, r_2, \dots, r_{N_e})$

Only M values are needed to represent $\rho(r)$

The density contains much less information than the wavefunction:

$$\rho(r) = N_e \int dr_2 dr_3 \dots dr_{N_e} \left| \Psi(r, r_2, r_3, \dots, r_{N_e}) \right|^2$$

The quantity of interest here is the total ground-state energy E of a many electron system: is the density alone sufficient to specify it completely?

$$\hat{H}\Psi = E\Psi$$

$$\hat{H} = \sum_i \frac{-\nabla_i^2}{2} + \sum_{i,I} \frac{-Z_I}{|r_i - R_I|} + \frac{1}{2} \sum_{i \neq j} \frac{1}{|r_i - r_j|}$$

(atomic units: $e = m = \hbar = 1$)

$$E = \text{Min}_{\Psi} \langle \Psi | \hat{H} | \Psi \rangle \quad \text{subject to} \quad \langle \Psi | \Psi \rangle = 1$$

To compute $\langle \Psi | \hat{H} | \Psi \rangle$ one needs $\rho_1(r; r')$ and $\rho_2(r_1, r_2; r_1, r_2)$

$$\rho_1(r; r') = N_e \int dr_2 dr_3 \dots dr_{N_e} \Psi^*(r, r_2, r_3, \dots, r_{N_e}) \Psi(r', r_2, r_3, \dots, r_{N_e}) \quad \text{etc.}$$

How can be possible to only use $\rho(r) \equiv \rho_1(r, r)$?

Approximate energy functionals of the density have been known since the early days of quantum mechanics (Thomas, Fermi, Dirac)

$$\text{For ex. } E \cong E_{TF}[\rho] = C_{TF} \int dr \rho(r)^{5/3}$$

It is, however, only after Hohenberg and Kohn that we know that the energy can be given (in principle) as an *exact* functional of the density

This is called the Hohenberg-Kohn theorem (*Phys. Rev. B* **136**, 864 (1964)):

$$E = \text{Min}_{\rho} E_V[\rho] \quad \text{subject to} \quad \int dr \rho(r) = N_e$$
$$E_V[\rho] = \int dr \rho(r)V(r) + \frac{1}{2} \int dr dr' \frac{\rho(r)\rho(r')}{|r-r'|} + F[\rho]$$

In practice we do not know $F[\rho] = \int dr \rho(r) f(r)$

We can, however, make a Local Density Approximation (LDA):

$$f(r) \approx f^{LDA}(\rho(r))$$

But this is not good enough to describe chemical bonding because it misses (like Thomas-Fermi) quantum shell effects

A solution to this difficulty was given by Kohn and Sham (*Phys Rev A* **140**, 1133 (1965))

Fictitious non-interacting electrons: KS equations

$$\rho(r) = 2 \sum_i |\psi_i(r)|^2 \quad \langle \psi_i | \psi_j \rangle = \delta_{ij}$$

$$E_V[\rho] = \int dr V(r) \rho(r) + \frac{1}{2} \int dr dr' \frac{\rho(r) \rho(r')}{|r - r'|} + 2 \sum_i \left\langle \psi_i \left| -\frac{\nabla^2}{2} \right| \psi_i \right\rangle + E_{XC}[\rho]$$

Euler-Lagrange equation for minimum: $\frac{\delta}{\delta \psi_i^*(r)} E_V[\rho] - 2 \sum_j \lambda_{ij} \psi_j(r) = 0$

$$\left(-\frac{\nabla^2}{2} + V(r) + \int dr' \frac{\rho(r')}{|r - r'|} + V_{XC}(r) \right) \psi_i(r) = \varepsilon_i \psi_i(r)$$

$V_{XC}(r) \equiv \frac{\delta E_{XC}}{\delta \rho(r)}$ is the exchange and correlation potential

$\hat{H}_{KS} \equiv -\frac{\nabla^2}{2} + V(r) + \int dr' \frac{\rho(r')}{|r - r'|} + V_{XC}(r)$ is the KS Hamiltonian

$\hat{H}_{KS}[\rho]\psi_i = \varepsilon_i\psi_i$ are self-consistent equations of the Hartree type

They can be solved by iterative diagonalization after representing the KS orbitals in a basis set:

$$\psi_i = \sum_{\alpha} C_{i\alpha} \varphi_{\alpha}$$

When *pseudopotentials* are used to eliminate core electrons a convenient basis set is constituted by plane waves:

$$\psi_{ik}(r) = \frac{1}{\sqrt{\Omega}} \sum_G c_{ik,G} e^{i(k+G)\cdot r} \quad (\text{where } k \in \text{BZ})$$

$$G \equiv \frac{2\pi}{L} (n_1, n_2, n_3) \quad \text{for a SC lattice}$$

Pseudopotentials: norm-conserving and ultrasoft

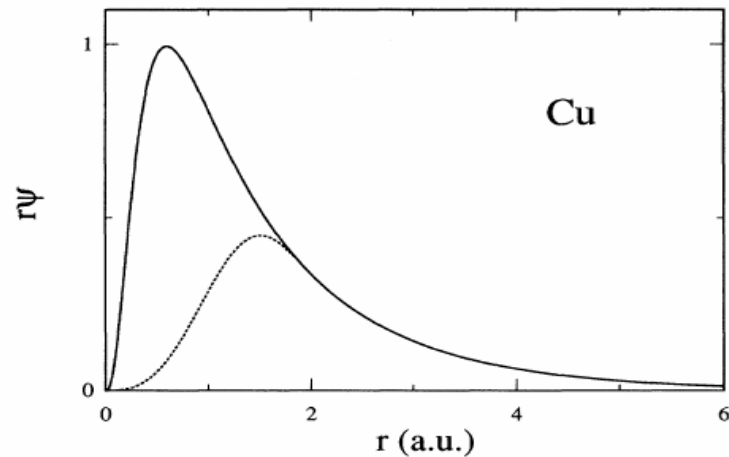


FIG. 1. All-electron (solid) and pseudo (dashed) radial wave functions of the 3d orbital of Cu. A cutoff radius of 2 a.u. has been used.

the example shows a ultrasoft pseudowavefunction

Pseudopotentials are effective potentials that mimic the combined effect of the nuclei and of the (frozen) core electrons on the valence (and conduction) electrons

In modern approaches (particularly with plane waves) self-consistent diagonalization is replaced by direct minimization

$$\text{Example: } \text{Min}_{\{x\}} F(\{x\})$$

$$\dot{x} = -\frac{\partial F}{\partial x} \quad \text{steepest descent}$$

$$\ddot{x} = -\frac{\partial F}{\partial x} - \gamma \dot{x} \quad \text{damped Newtonian dynamics}$$

Minimization of the KS energy functional by damped dynamics:

$$\ddot{\psi}_i = -\frac{\delta E_V[\rho]}{\delta \psi_i^*(r)} - \gamma \dot{\psi}_i(r) + 2 \sum_j \lambda_{ij} \psi_j(r)$$

$$\text{At minimum } (\dot{\psi} = \ddot{\psi} = 0) \text{ and } \frac{\delta}{\delta \psi_i^*(r)} E_V[\rho] - 2 \sum_j \lambda_{ij} \psi_j(r) = 0$$

Given $E = \text{Min}_\rho E_V[\rho]$ for a nuclear configuration $\{R\} \equiv (R_1, R_2, \dots, R_{N_I})$

the Born-Oppenheimer (BO) Potential Energy Surface is given by:

$$\Phi(\{R\}) = E + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J}{|R_I - R_J|}$$

By optimizing $\Phi(\{R\})$ we obtain equilibrium atomic structures

From the Hessian of Φ we construct the dynamical matrix whose eigenvalues/eigenvectors are the vibrational frequencies/normal modes, etc.

How well does DFT compare with experiment (and with highly accurate quantum chemical calculations for small molecules)?

The accuracy of DFT is determined by the accuracy of the approximated form used for the XC energy functional.

Currently most calculations of extended systems (e.g. materials) and large molecules use the Generalized Gradient Approximation (GGA):

$$E_{XC}^{LDA}[\rho] = \int dr \rho(r) \varepsilon_{XC}^{LDA}(\rho(r)) \quad E_{XC}^{GGA}[\rho] = \int dr \rho(r) \varepsilon_{XC}^{GGA}(\rho(r), \nabla \rho(r))$$

A popular GGA form is the PBE functional (Perdew, Burke, Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996))

GGA does rather well with most interatomic interactions with the exception of Van der Waals interactions

Structural Relaxation by simultaneous relaxation of electronic and atomic coordinates

$$M\ddot{R}_I = -\frac{\partial E[\{R\}, \{\psi\}]}{\partial R_I} - \gamma_a M\dot{R}_I$$

$$\mu\ddot{\psi}_n = -\frac{\delta E[\{R\}, \{\psi\}]}{\delta \psi_n^*} - \gamma_e \mu\dot{\psi}_n + \sum_m \Lambda_{nm} \psi_m$$

First-Principles Molecular Dynamics

Molecular Dynamics (MD) is powerful statistical mechanical technique in which classical atomic trajectories are integrated numerically

$$M_I \ddot{R}_I = -\frac{\partial \Phi}{\partial R_I} \quad \langle G(\{R\}) \rangle = \frac{1}{T} \int_0^T dt G(\{R(t)\})$$

First-Principles MD combines MD with DFT, using a DFT potential energy surface to generate atomic trajectories.

It relies on the BO separation of nuclear and electronic dynamics, assuming classical mechanics for the former.

BO Potential Energy Surface:

$$\Phi(\{R\}) = \text{Min}_{\{\psi\}} E_{V(\{R\})}[\{\psi\}] + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J}{|R_I - R_J|}$$

Performing a new functional minimization at each time step is expensive. Car and Parrinello (*Phys Rev Lett* **55**, 2471 (85)) proposed to use instead:

$$\tilde{\Phi}[\{\psi\};\{R\}] = E_{V(\{R\})}[\{\psi\}] + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J}{|R_I - R_J|}$$

Minimization is achieved dynamically in the CP equations by separation of the time scales of electronic and nuclear motion.

This significantly more efficient.

CP equations:

$$M_I \ddot{R}_I = - \frac{\partial \tilde{\Phi} [\{R\}, \{\psi\}]}{\partial R_I}$$
$$\mu \ddot{\psi}_n = - \frac{\delta \tilde{\Phi} [\{R\}, \{\psi\}]}{\delta \psi_n^*} + \sum_m \Lambda_{nm} \psi_m$$

With appropriate choice of μ and initial conditions the electrons are faster than nuclear motion, and on the time scale of the latter:

$\overline{\tilde{\Phi}} \approx \Phi$ Then CP dynamics is a good approximation of BO dynamics.

In this approach the fictitious non-interacting electrons of DFT become fictitious classical dynamical fields.