Electronic Structure Methodology 2

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Lecture Three

The Kohn-Sham Equations

$$E_{\mathrm{tot}}[\{\psi_i\}] = -2\sum_i \frac{\hbar^2}{2m}\int \psi_i \nabla^2 \psi_i d\mathbf{r}$$
$$+ \int V_{\mathrm{ion}}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r}$$
$$+ \frac{e^2}{2}\int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$$
$$+ E_{\mathrm{xc}}[n(\mathbf{r})] + E_{\mathrm{ion}}(\mathbf{R_i})$$

The charge density is written as:

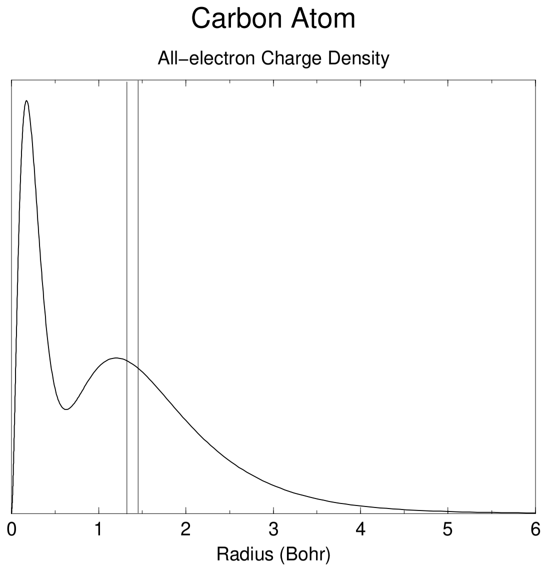
$$n(\mathbf{r}) = 2\sum_i |\psi_i(\mathbf{r})|^2$$

The potentials are given by *functional* derivatives:

$$V_{\mathrm{xc}}(\mathbf{r}) = \frac{\delta E_{\mathrm{xc}}[n(\mathbf{r})]}{\delta n(\mathbf{r})} \text{ etc.}$$

$$\boxed{[-\frac{\hbar^2}{2m}\nabla^2 + V_{\mathrm{ion}}(\mathbf{r}) + V_{\mathrm{H}}(\mathbf{r}) + V_{\mathrm{xc}}(\mathbf{r})]\psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r})}$$

Core and Valence electrons

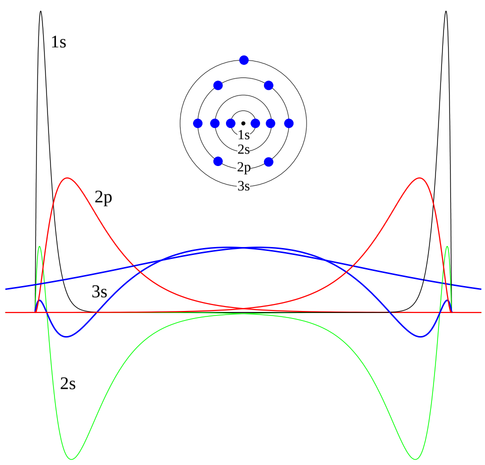


- Core electrons don't take part in bonding (definition!)

Level	Energy(Ry)	Occupation
1s	-19.90408	2.000
2s	-1.00279	2.000
2p	-0.39838	2.000

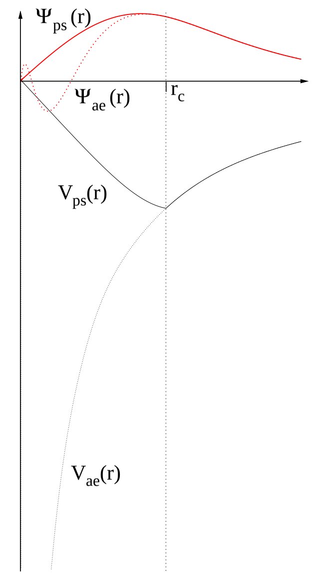
- To avoid calculating the properties of the (possibly many) core electrons we can invent *pseudopotentials*

The Pseudopotential Approach



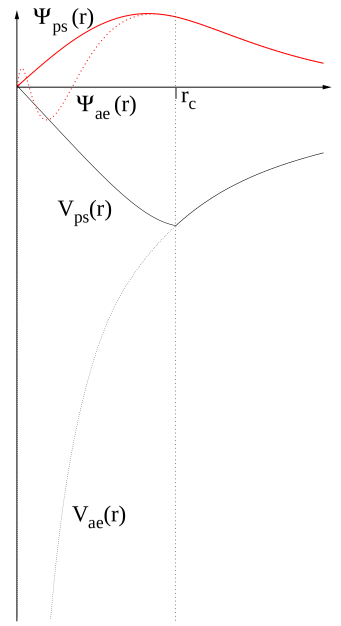
- The pseudopotential was originally thought of as the weaker effective potential due to the orthogonality of the valence to the core wavefunctions
- This concept provided a justification and theoretical framework for the nearly free electron approximation
- The true power of the method unleashed by much later *ab initio* formulations

The Pseudopotential Scheme



- Do an all electron atomic calculation
- Choose a core radius, and *pseudise* the atomic wavefunctions in the channels of interest
- The simplest schemes conserve the *norm* but this can be relaxed
- Invert the Schrödinger equation to find the *pseudopotential*

The Pseudopotential Scheme

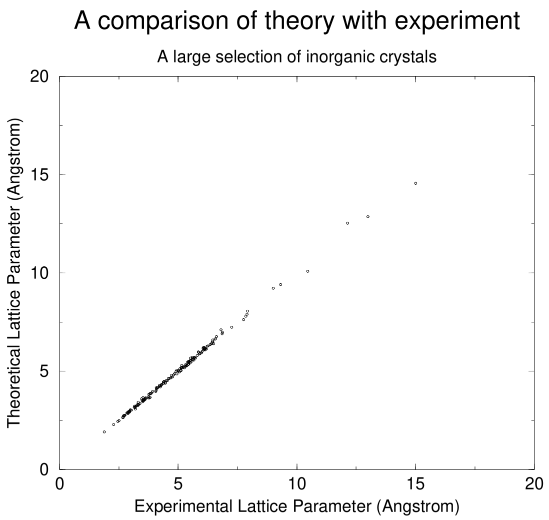


- The resulting pseudopotential will reproduce the *reference* eigenstates by construction, and is nonlocal in general
- *Transferability* is of great importance – the potentials should be tested extensively
- There may be *ghost states*

It Works!

Material	Expt	Theory	Delta	Type
LaBi	6.57	6.648	1.2%	alloy
CaF_2	5.4626	5.496	0.6%	halide
Ag	4.086	4.112	0.6%	metal
V	3.028	3.019	-0.3%	metal
ZrN	4.62	4.634	0.3%	misc
NbO	4.2103	4.2344	0.6%	oxide
GaAs	5.653	5.663	0.2%	semiconductor
$CoSi_2$	5.36	5.3	-1.1%	silicide

A reminder



- We got all this from
  - Schrödinger's Equation
  - Density functional theory
  - a many-body uniform electron gas
  - some clever approximations

Milman, Winkler, White, Pickard, Payne, Akhmatskaya, and Nobes.

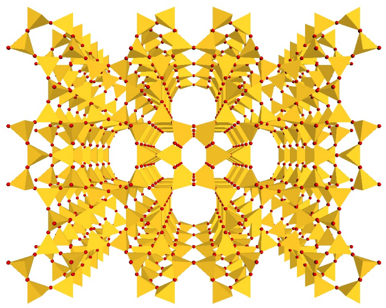
Electronic structure, properties and phase stability of inorganic crystals:

The pseudopotential plane-wave approach.

International Journal of Quantum Chemistry, **77**:895-910, 2000.

We made lots of progress but . . .

. . . these approximations are not enough to allow calculations for large systems



Ferrierite

- Conventional matrix diagonalisation
  - too slow for a large, well converged, basis set
  - calculates too many (unoccupied) states
- The unoccupied states do not contribute to the total energy, so why calculate them?

Calculating the total energy

1. Eigenvalue term
2. Potential term
3. Ion-ion term

To get eigenvalues we use:

$$H|\psi_i\rangle = \epsilon_i|\psi_i\rangle$$

$$H = -\frac{1}{2}\nabla^2 + V(\mathbf{r})$$

- Most stable computational approach is to directly minimise the total energy
- Do not solve $H|\psi_i\rangle = \epsilon_i|\psi_i\rangle$ directly
- Use iterative diagonalisation for just the states that we need
- We still need to operate H on $|\psi_i\rangle$

Operating with H on $|\psi_i\rangle$

- H divides into two parts
  - The potential — diagonal in real space
  - The kinetic energy — diagonal in reciprocal space
- Could use FFTs (Fast Fourier Transforms) and evaluate each term in appropriate space
- The potential $V(\mathbf{r})$ can be evaluated in real space
- Kinetic energy in reciprocal space — $\frac{1}{2}|\mathbf{k}+\mathbf{G}|^2$ if we use a plane wave basis set (more on this later)
- Different basis sets suggest different strategies

Evaluating the Energy

- The eigenvalue sum:

  $\epsilon_i = \langle\psi_i|H|\psi_i\rangle$

- Potential energy — product of potential with density, then integrate :

  $E_{\mathrm{pot}} = \int V(\mathbf{r})n(\mathbf{r})d\mathbf{r}$

- $E_{\mathrm{ion-ion}}$ converges slowly in both real and reciprocal space so use the Ewald identity
  - splits the sum between two spaces
  - the sum of the terms converges rapidly

Iterative Diagonalisation

- Need energy gradient for each band i and iteration m:

$$|\eta_i^m\rangle = -(H - \epsilon_i^m)|\psi_i^m\rangle$$

$$\epsilon_i^m = \langle\psi_i^m|H|\psi_i^m\rangle$$

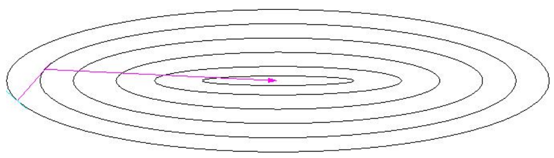
- Antisymmetry of wavefunctions $\rightarrow$ orthogonality of bands at each k-point

- Enforce orthogonality via the gradient:

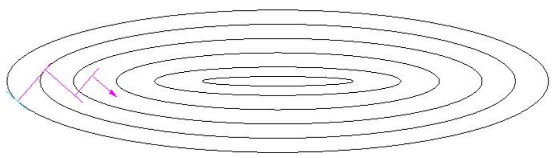
$$|\eta'^m_i\rangle = |\eta_i^m\rangle - \sum_j \langle\psi_j|\eta_i^m\rangle|\psi_j\rangle$$

- Orthogonalisation is costly and dominates in the limit of a very large system

Minimisation



- Steepest descents — safe, but very slow



- Conjugate gradients — use history to ensure independence (exact for quadratic functions)
- Preconditioning — to encourage all components of the wavefunction to converge at comparable rates