Electronic Structure Methodology 1

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Lecture Two
In the last lecture we learnt how to write the total energy as a functional of the density $n(r)$:

$$E_{\text{tot}} = \int dr v(r)n(r) + T[n] + E_H[n] + E_{xc}[n]$$

But, just as for the $E_{xc}[n]$ we don’t know what this functional $T[n]$ is.

As for $E_{xc}[n]$, guesses can be made (e.g. Thomas-Fermi), but they are not good enough.

$T[n]$ was introduced as the kinetic energy of a system of non-interacting electrons with a density of $n(r)$.

We must write $T[n]$ explicitly in terms of the independent electron Kohn-Sham orbitals.
The Kohn-Sham Equations

\[ E_{\text{tot}}[\{\psi_i\}] = -2 \sum_i \frac{\hbar^2}{2m} \int \psi_i \nabla^2 \psi_i d\mathbf{r} \]

\[ + \int V_{\text{ion}}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} \]

\[ + \frac{e^2}{2} \int \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \]

\[ + E_{\text{xc}}[n(\mathbf{r})] + E_{\text{ion}}(\mathbf{R}_i) \]

The charge density is written as:

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

The potentials are given by functional derivatives:

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

\[ \left[ -\frac{\hbar^2}{2m} \nabla^2 + V_{\text{ion}}(\mathbf{r}) + V_H(\mathbf{r}) + V_{\text{xc}}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}) \]
The Kohn-Sham Orbitals

- The Kohn-Sham orbitals were introduced so that we can compute the independent electron kinetic energy corresponding to a charge density $n(r)$.

- They need not have any physical meaning, nor need the Kohn-Sham eigenvalues.

- However, experience shows that they do have some correspondence to the quasi-particle energy levels probed by spectroscopic techniques.

- The so-called “band-gap problem”, to a good approximation, simply results in a rigid shift of the unoccupied energy levels.
Dielectric Properties of Diamond

The complex dielectric function for diamond was calculated with a 0.7ev Scissor operator applied to the conduction bands.
Being (self) consistent

- $V_H(r)$ and $V_{XC}(r)$ depend on $n(r)$
- $n(r)$ depends on $\{\psi_i(r)\}$
- But we are trying to find $\{\psi_i(r)\}$ and the corresponding energy levels — we need self-consistency
Solving an eigenproblem in a basis

- We have a problem of the form:
\[ \hat{H} |\psi_i\rangle = \epsilon_i |\psi_i\rangle \]

- The wavefunctions are orthonormal:
\[ \langle \psi_i | \psi_j \rangle = \delta_{ij} \]

- If we choose a basis, we can construct a Hamiltonian as a matrix and diagonalise that matrix to get the eigenvectors and eigenvalues:
\[ H_{ij} = \langle v_i | \hat{H} | v_j \rangle \]

energy level → eigenvalue

wavefunction → eigenvector
Just a few atoms

- Use a local basis set
  - possibly based on atomic orbitals
  - maybe some mathematically simple set like gaussians
- Build the Hamiltonian matrix
- Diagonalise
- This scales at $O(N^3)$
The electrons in a crystal experience a potential with the periodicity of the Bravais lattice: \( U(\mathbf{r} + \mathbf{R}) = U(\mathbf{r}) \)

- The scale of the periodicity is of the order of the de Broglie wavelength of an electron — 1Å— so we must use Quantum Mechanics.

- Of course, the periodicity is an idealisation: impurities, defects, thermal vibrations, finite size effects.
IN A CRYSTAL

- Crystals contain $\approx 10^{23}$ atoms

- Direct diagonalisation of even a cluster of $10^3$ atoms would be very costly

- So is it impossible?

- No!! Use symmetry . . .

  - crystals have translational symmetry (definition)
  - symmetry leads to a new quantum number, $k$
  - use periodic boundary condition (PBCs) and you just have to worry about the atoms in the unit cell of the crystal
**Periodic boundary conditions and Bloch’s Theorem**

Independent electrons which obey the one electron Schrödinger equation for a periodic potential are called *Bloch electrons* and obey Bloch’s theorem.

- Bloch’s theorem can be written in two equivalent forms.
The First Brillouin Zone

The wave vector $\mathbf{k}$ can always be confined to the first Brillouin zone (or any primitive cell of the reciprocal lattice).

Any $\mathbf{k}'$ not in the first Brillouin zone can be written as: $\mathbf{k}' = \mathbf{k} + \mathbf{K}$, where $\mathbf{k}$ is in the first Brillouin zone and $e^{i\mathbf{K} \cdot \mathbf{R}} = 1$.

The labels K,L,W,X and $\Gamma$ are high symmetry points in the Brillouin zone.
Integrating Over The First Brillouin Zone

- Observables are calculated as integrals over all \( k \)-points within the first Brillouin zone:

\[
E_{\text{tot}} = \frac{1}{V_{\text{BZ}}} \int_{1^{\text{st}} \text{BZ}} E(k) \, dk
\]

\[
n(r) = \frac{1}{V_{\text{BZ}}} \int_{1^{\text{st}} \text{BZ}} n_k(r) \, dk
\]

- The integrals for metals are more difficult to converge
Defining the k-Point Grid

- The symmetry of the cell can be used to reduce the number of k-points needed to obtain convergence
- Shifting the origin of the grid can improve the convergence with the number of k-points
- The larger the unit cell used, generally the fewer k-points that are required to achieve convergence (but there are more bands)
**Band Structure**

- For a given \( \mathbf{k} \) there many solutions to the Schrödinger equation:
  \[
  H_\mathbf{k} \psi_\mathbf{k} = E_\mathbf{k} \psi_\mathbf{k}(\mathbf{r}), \psi_\mathbf{k}(\mathbf{r}) = \psi_\mathbf{k}(\mathbf{r} + \mathbf{R})
  \]

- The boundary conditions ensure that there are many (labelled \( n \)) discretely spaced eigenvalues

- The Hamiltonian depends on \( \mathbf{k} \) as a parameter, and so the eigenvalues vary continuously with wave vector for a given \( n \). Hence, they are *bands*
Beyond Translational Symmetry in Crystals

There can be other symmetries in addition to translational symmetry.

The subject of crystallography systematises the classification of these different symmetries.

The number of possibilities can be shown to be finite for crystals, and have been enumerated.

The symmetries of a cube are identical to an octahedron, but not a tetrahedron.
**The Super-cell approximation**

- Acell is chosen that mimics the aperiodic behaviour, but the periodic boundary conditions remain.
- This is the *super-cell*.
- The super-cell chosen must be large enough that the properties of interest are converged with respect to cell size.

- Aperiodic systems can also be treated within periodic boundary conditions.

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Point Defect  Adsorption on Surface