Electronic structure calculation methods using the Density Functional Theory

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Goal

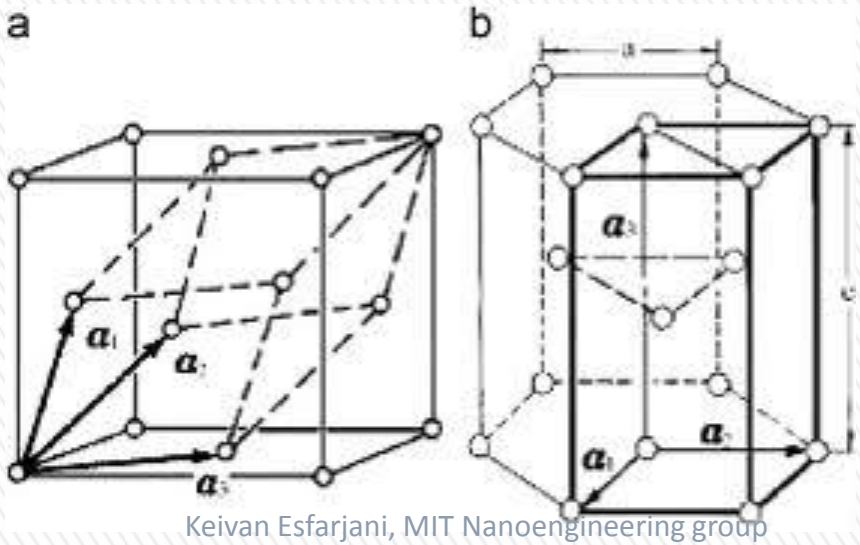
» To calculate all the properties of a molecule or crystalline system knowing its atomic information:

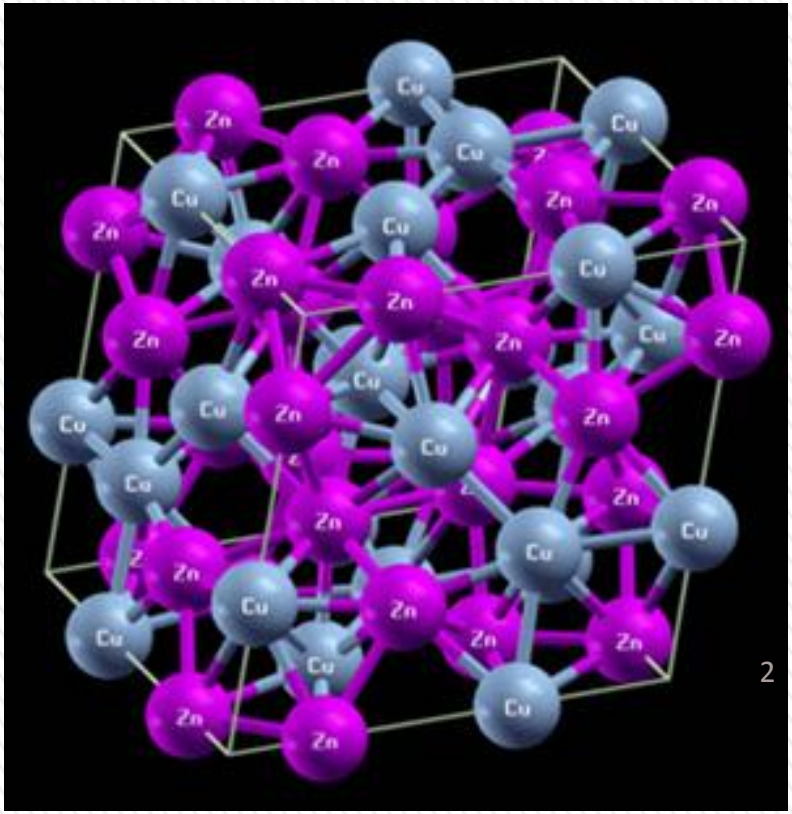
> Atomic species

> Their coordinates

> The Symmetry

> The primitive (unit) cell





Theoretician's goal

Calculate the ground state many-body wavefunction, and the total energy

$$\Psi_\lambda(r_1,\ldots,r_N), E_\lambda$$

Solutions to the MB Schroedinger's equation:

$$H(r_1,\ldots,r_N)\,\Psi_\lambda(r_1,\ldots,r_N) = E_\lambda\,\Psi_\lambda(r_1,\ldots,r_N)$$

… and eventually the lowest excited states

Relation to the physical Properties?

> **Most** properties of interest can be expressed as derivatives of the total energy

> Transport (electrical and thermal conductivity)

> Magnetic (susceptibility, magnetization)

> Optical (band gap, dielectric constant, …)

> Elastic (elastic constants)

> Thermodynamic (Cv, α, γ)

> … and other **RESPONSE FUNCTIONS** , which can be expressed as: $\partial^2 E / \partial A \partial B$

Total Energy

» Central quantity defining the ground state

» Generalized "forces" (1st derivatives)

> magnetization, charge density: wrt B, V

> Forces on atoms: wrt atomic displacement

> Electron affinity and Ionization potential: wrt N

» Generalized "Susceptibilities" (2nd derivatives)

> Hardness: wrt Volume

> Bandgap (chemical hardness): wrt electron number

> Magnetic susceptibility: wrt B-field

EA,IP, Chemical potential and the bandgap

$$EA = -E(N+1) + E(N) \approx -\varepsilon_{N+1}$$

$$IP = -E(N) + E(N-1) \approx -\varepsilon_{N}$$

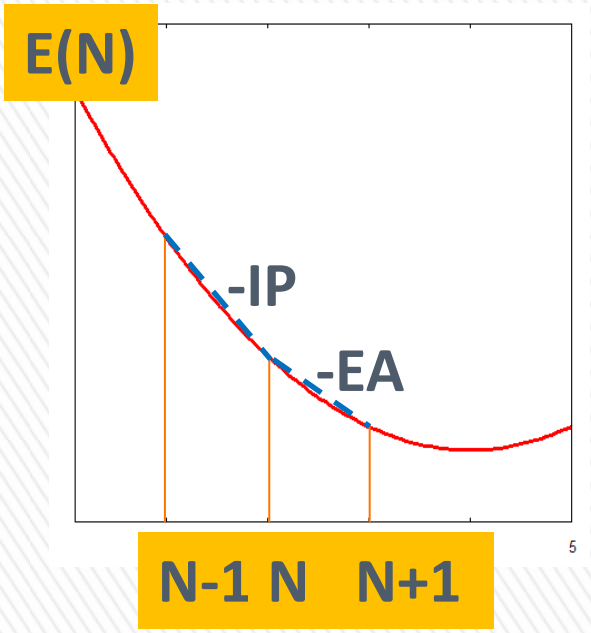
$$\mu = \partial E / \partial N \approx -(EA + IP)/2$$

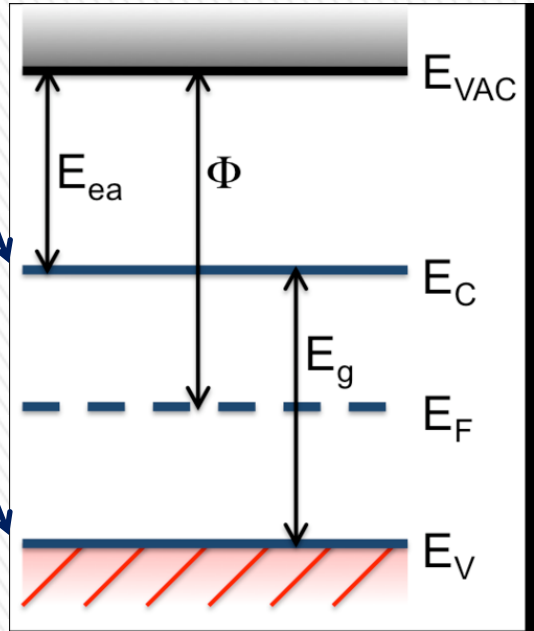
$$E_{Gap} = \partial^2 E / \partial N^2$$

$$\approx E(N+1) + E(N-1) - 2E(N)$$

$$\approx IP - EA$$

Electronegativity (Mulliken)





The Many-body problem

$$\hat{H} = \hat{T}_e + \hat{V}_{ne} + \hat{V}_{ee} + \hat{V}_{nn}$$

$$= -\frac{\hbar^2}{2m_e}\sum_i^{N_e}\nabla_i^2 + \frac{e^2}{4\pi\epsilon_0}\left[-\sum_i^{N_e}\sum_I^{N_n}\frac{Z_I}{|\vec{r}_i - \vec{R}_I|} + \frac{1}{2}\sum_i^{N_e}\sum_{j\neq i}^{N_e}\frac{1}{|\vec{r}_i - \vec{r}_j|} + \frac{1}{2}\sum_I^{N_n}\sum_{J\neq I}^{N_n}\frac{Z_I Z_J}{|\vec{R}_I - \vec{R}_J|}\right]$$

» **Dynamics**: Born-Oppenheimer approximation

Due to their fast dynamics compared to ionic motion, electrons stay at all times in their ground state (the BO surface)

Difficulty

» The many-body wavefunction is a function of 3N coordinates (for an N-electron system)

$$H(r_1,\ldots,r_N)\,\Psi_\lambda(r_1,\ldots,r_N) = E_\lambda\,\Psi_\lambda(r_1,\ldots,r_N)$$

» Mean-field idea: one electron is moving in the "average field" created by N-1 other electrons also called independent electron approximation

⇒Reduces the problem to a one-body one with only 3 coordinates in the wavefunction

⇒Works at higher dimensions due to reduced quantum fluctuations

$$A = \langle A \rangle + (A - \langle A \rangle) \quad \langle f(A) \rangle \approx f(\langle A \rangle) + O\left(\sigma_A^2 f''(\langle A \rangle)\right)$$

Solution method

» No exact solution!

» Approximation methods: Variational method

An approximation to the ground state can be found by minimizing E_{var}

$$E_0 \leq E_{var} = \int \Psi^*_{guess} \, H \, \Psi_{guess} \, dr_1 \ldots dr_N$$

Need to **assume a form** for the variational wavefunction

Mean-field approximation

- **Reduce the many-body problem to a one-body problem**
- What is the "best" mean field? How do we define it?
- Guess: Electrostatic field:
  - > Hartree Approximation (1927)
- Add exchange effects due to fermion statistics (Pauli):
  - > Hartree-Fock Approximation (1928)
- Density-functional Theory (1964)

Mean-field (H-HF)

» Hartree: the N-electron WF is a product of one-electron WFs

$$\Psi_\lambda(r_1,\ldots,r_N) = \chi_1(r_1)\times\ldots\times\chi_N(r_N)$$

» Hartree-Fock: the N-electron WF is an antisymmetric product of one-electron WFs

$$\Psi_\lambda(r_1,\ldots,r_N) = \frac{1}{\sqrt{N!}}\sum_{\text{permuation}\,\sigma}(-1)^\sigma\chi_{\sigma(1)}(r_1)\times\ldots\times\chi_{\sigma(N)}(r_N)$$

It can also be written as a Slater determinant, which manifestly satisfies Pauli

$$\Psi(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_N) = \frac{1}{\sqrt{N!}}\begin{vmatrix}\chi_1(\mathbf{x}_1) & \chi_2(\mathbf{x}_1) & \cdots & \chi_N(\mathbf{x}_1)\\ \chi_1(\mathbf{x}_2) & \chi_2(\mathbf{x}_2) & \cdots & \chi_N(\mathbf{x}_2)\\ \vdots & \vdots & \ddots & \vdots\\ \chi_1(\mathbf{x}_N) & \chi_2(\mathbf{x}_N) & \cdots & \chi_N(\mathbf{x}_N)\end{vmatrix}$$

Mean-field (H-HF)

» If the total energy is minimized wrt χ_λ, with the normality constraint, then the resulting equations satisfied by χ_λ, are called the Hartree/HF equations.

The HF equations

obtained after **minimization** of the variational energy

$$\partial(\mathrm{E}_{\mathrm{var}} - \mathrm{Constraint}) / \partial\chi^{*}_{\lambda\sigma} = 0 \Rightarrow \mathrm{H}^{\sigma}\chi_{\lambda\sigma}(\mathrm{r}) = \mathrm{E}_{\lambda\sigma}\chi_{\lambda\sigma}(\mathrm{r})$$

E's are Lagrange multipliers coming from the normalization constraint

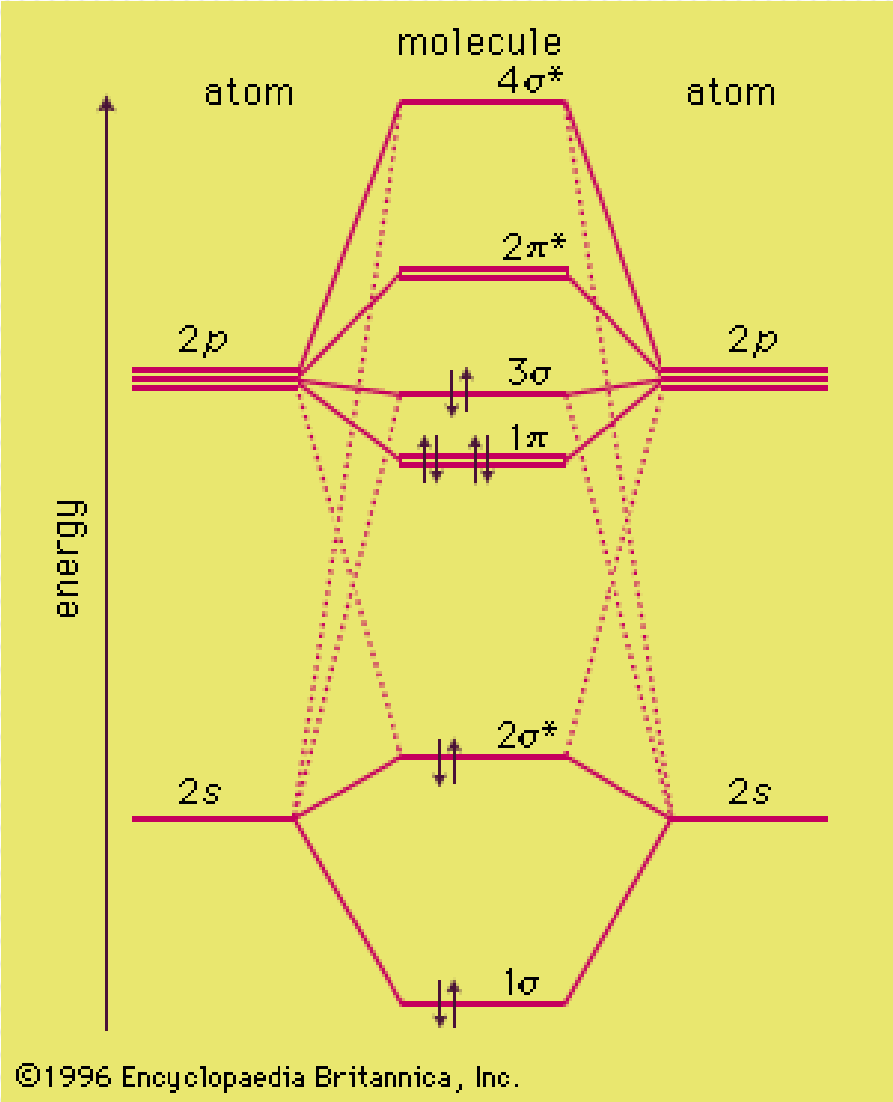
$$H^{\sigma} = \frac{p^2}{2m} + V_{ion}(r) + V_{Coulomb}(r) + V^{\sigma}_{exchange}(r)$$

$$\mathrm{V}_{\mathrm{Coulomb}}(\mathrm{r}) = \sum_{\mu\sigma'}^{\mathrm{occupied}} \int \frac{\chi^{*}_{\mu\sigma'}(\mathrm{r}')\chi_{\mu\sigma'}(\mathrm{r}')}{|\mathrm{r}-\mathrm{r}'|}\mathrm{dr}' = \int \frac{\rho(\mathrm{r}')}{|\mathrm{r}-\mathrm{r}'|}\mathrm{dr}'$$

$$\mathrm{V}^{\sigma}_{\mathrm{exchange}}(\mathrm{r})\chi_{\lambda\sigma}(\mathrm{r}) = \sum_{\mu\sigma'}^{\mathrm{occupied}} \delta_{\sigma\sigma'} \int \frac{\chi^{*}_{\mu\sigma'}(\mathrm{r}')\chi_{\lambda\sigma}(\mathrm{r}')}{|\mathrm{r}-\mathrm{r}'|}\mathrm{dr}'\,\chi_{\mu\sigma'}(\mathrm{r})$$

Energy level diagram

Ground state
defined by
occupied states



Shortcomings of HF

» "Underbinds" molecules (by typically 10%)

» Over-estimates the gap by a factor of 2

» Predicts a "pseudo-gap" for the jellium model

⇒Due to a lack of electron **screening**

The exchange potential (or single Slater determinant) does not tell the whole story!

We need to add other electronic configurations to the wavefunction to better describe screening

DFT

- Due to Hohenberg and Kohn (1964) and Kohn-Sham (1965) who formulated the variational problem:
- If the ground state density is defined as:

$$\rho(r) = N\int |\Psi(r, r_2, \ldots, r_N)|^2 \, dr_2 \ldots dr_N$$

- There is a **one to one correspondence** between the ground state charge density and the many-body wavefunction. E_o is a UNIQUE functional of the ground state density

$$V_{ext}, E_o <-> \Psi_o(r_1, \ldots, r_N) -> \rho_o(r)$$

$$V_{ext} -> \Psi_o(r_1,...,r_N) -> \rho_o(r)$$

» Can two different external potentials produce the **same** (non-degenerate) ground state density?

$$H = T + V_{ee} + V_{ext}$$

Take V1 and V2 leading to H1 and H2 and Ψ1 and Ψ2

$$\langle \Psi_1 | H_1 | \Psi_1 \rangle = E_1 < \langle \Psi_2 | H_1 | \Psi_2 \rangle = E_2 + \langle \Psi_2 | V_1 - V_2 | \Psi_2 \rangle$$

$$\text{but} \langle \Psi_2 | V_1 - V_2 | \Psi_2 \rangle = \int \rho_o(r)[v_1(r) - v_2(r)]dr$$

$$\text{likewise } E_2 < E_1 + \langle \Psi_1 | V_2 - V_1 | \Psi_1 \rangle = E_1 + \int \rho_o(r)[v_2(r) - v_1(r)]dr$$

$$\text{implying } E_1 + E_2 < E_2 + E_1$$

$$\Psi_o(r_1,...,r_N) <- V_{ext} <- \rho_o(r)$$

$$=> \Psi_o = \Psi[\rho_o]$$

$$=> E_o = \mathrm{Min}_\rho E[\rho] = E[\rho_o]$$

DFT…

» E_o is obtained by minimizing this functional $E[\rho]$ wrt ρ with the constraint that

$$\int \rho(\mathrm{r})\,\mathrm{dr} = \mathrm{N}$$

» Kohn&Sham derived the resulting one-body Schroedinger-like equations bearing their name

Kohn-Sham equations

Solve self – consistently

$$H_{KS}[\rho]\,\psi_\lambda = \varepsilon_\lambda\,\psi_\lambda \;;\; \rho(r) = \sum_{\lambda}^{\text{occupied}} |\psi_\lambda(r)|^2$$

$$H_{KS}[\rho] = \frac{p^2}{2m} + v_{ext}(r) + v_{Coulomb}[\rho(r)] + v_{xc}[\rho(r)]$$

with $v_{xc}[\rho(r)] = \delta E_{xc} / \delta\rho(r)$ and

$$E[\rho] = T + E_H + E_{xc} + E_{ext}$$

Total Energy functionals

$$E[\rho] = T + E_H + E_{xc} + E_{ext}$$

$$E_{ext} = \int v_{ext}(r)\,\rho(r)\,dr$$

$$E_H = \frac{1}{2}\int \frac{\rho(r)\rho(r')}{|r - r'|}\,dr\,dr'$$

$$T[\rho] = \left\langle \sum_i \frac{p_i^2}{2m} \right\rangle \quad \text{and} \quad E_{xc}[\rho] = \langle V_{ee} \rangle - E_H \;??$$

$$T_{TF}[\rho] = C\int \rho^{5/3}(r)\,dr$$

$$E_x^{Jellium}[\rho] = -D\int \rho^{4/3}(r)\,dr$$

Thomas-Fermi-Dirac functional

DFT…

- So in order to get the GROUND STATE energy and electron density, one needs to minimize $E[\rho]$, or in other words, solve the KS equations.
- Most physical properties are then obtained from finite differences of this GS energy.
- Approximation: the mysterious XC energy functional and the resulting XC potential
- Caveat: ONLY ρ_o and E_o are supposed to be correct!

Local Density Approximation (LDA)

» Also proposed by HK (1964)

$$E_{XC}^{LDA} = \int \rho(r)\, e_{XC}(r)\, dr = \int \rho(r)\, e_{XC}^{hom}[\rho(r)]\, dr$$

Uses the XC energy density of the Jellium model calculated numerically "exactly" by QMC: $V_{xc} = V_{xc}(\rho)$

» It satisfies the xc-hole sum rule, explaining its success.

$$E_{XC}^{LSDA} = \int \rho(r)\, e_{XC}[\rho_\uparrow(r), \rho_\downarrow(r)]\, dr \quad \text{with} \quad \rho_\downarrow + \rho_\uparrow = \rho$$

$$v_{xc}^{\sigma}(r) = \partial E_{XC}^{LSDA}[\rho_\uparrow, \rho_\downarrow] / \partial \rho_\sigma(r)$$

Shortcomings of DFT

» Overestimates binding energies (≈ by 15%)

» Underestimates the gap (≈ by 40%)

» "Good" for solids but "bad" for molecules

Overscreens, since functionals are taken from Jellium model

But surprisingly successful in predicting the correct crystal structure and elastic constants (<5% error) for a large variety of systems.

Beyond DFT and one-electron theories

- **GW method:** Many-body perturbation theory, take DFT GS as reference unperturbed and the rest of Coulomb interactions as perturbation
  - Solves the screening problem and produces correct band gaps
- **Quantum Monte Carlo:** Very accurate solution to the ground state energy and MB-WF
- **Configuration-Interaction:** Diagonalize the MB Hamiltonian in the basis formed of Slater determinants of occupied and unoccupied states (chemists method of choice, used for molecules)