Introduction to Density Functional Theory (part I)

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Wave Function theory

(aka. Electronic structure theory)

Electron density

dipole moment,
charge distribution,…

Electronic energy

Born-Oppenheimer
approximation 1927

Potential energy surface (PES)

☐ Molecular geometry
☐ Bond energies
☐ Barrier heights
☐ Spectra

Schrödinger wavefunction

- **Wave Function Theory (WFT)** define by Erwin Schrödinger (1925)
- Awarded the Nobel Prize in Physics (1933) for his work on WFT
- Electron cannot be describes by classical mechanics
- Described in term of wavefunction Ψ (all the information is contained in the wavefunction)
- Time independent Schrödinger equation describes the particle wave duality

$$\widehat{\boldsymbol{H}}\Psi = \widehat{\boldsymbol{E}}\Psi$$

- For a general N particle system the Hamiltonian operator contains both Kinetic ($\hat{T}$) and Potential ($\hat{V}$) energy terms for all particles

Hamiltonian

$$\nabla_{r_i}^2 = \frac{\delta^2}{\delta x_i^2} + \frac{\delta^2}{\delta y_i^2} + \frac{\delta^2}{\delta z_i^2}$$

The Hamiltonian is define as:

$$\hat{H} = \hat{T}_N + \hat{T}_e + \hat{V}_{Ne} + \hat{V}_{ee} + \hat{V}_{NN}$$

Schrödinger equation can be separated into two parts based on the Born-Oppenheimer approximation.

The Born-Oppenheimer approximation states:
Nuclei are much heavier and much much slower than electrons. So for practical purposes it is convenient to decouple the nuclear and electronic motion to compute electronic energies for “fixed” nuclear positions.

Nuclear Equation

$$\hat{H} = \hat{T}_N + \hat{V}_{NN}$$

$$\hat{T}_N = -\sum_i \frac{-\hbar^2}{2M_i} \nabla_{R_i}^2 \qquad \hat{V}_{NN} = \sum_i \sum_{j>i} \frac{Z_i Z_j e^2}{4\pi\varepsilon_0 |R_i - R_j|}$$

The Born-Oppenheimer approximation sets $T_N = 0$.

Electronic Equation

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

$$\hat{T}_e = -\sum_i \frac{-\hbar^2}{2m_e} \nabla_{r_i}^2 \qquad \hat{V}_{Ne} = -\sum_i \sum_j \frac{Z_i e^2}{4\pi\varepsilon_0 |R_i - R_j|}$$

$$\hat{V}_{ee} = \sum_i \sum_{j>i} \frac{e^2}{4\pi\varepsilon_0 |r_i - r_j|}$$

The Electronic Hamiltonian

- Considering a single nuclei system where $\hat{V}_{NN}$ can be ignored
- Which can be generalized as $\hat{H} = \hat{T}_e + \hat{V}_{Ne} + \hat{V}_{ee}$

Electronic Equation for 2 electron system in atomic units

$$\hat{H} = \underbrace{-\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2}_{\hat{T}_e} \underbrace{- \frac{Z}{r_1} - \frac{Z}{r_2}}_{\hat{V}_{Ne}} \underbrace{+ \frac{1}{r_{12}}}_{\hat{V}_{ee}}$$

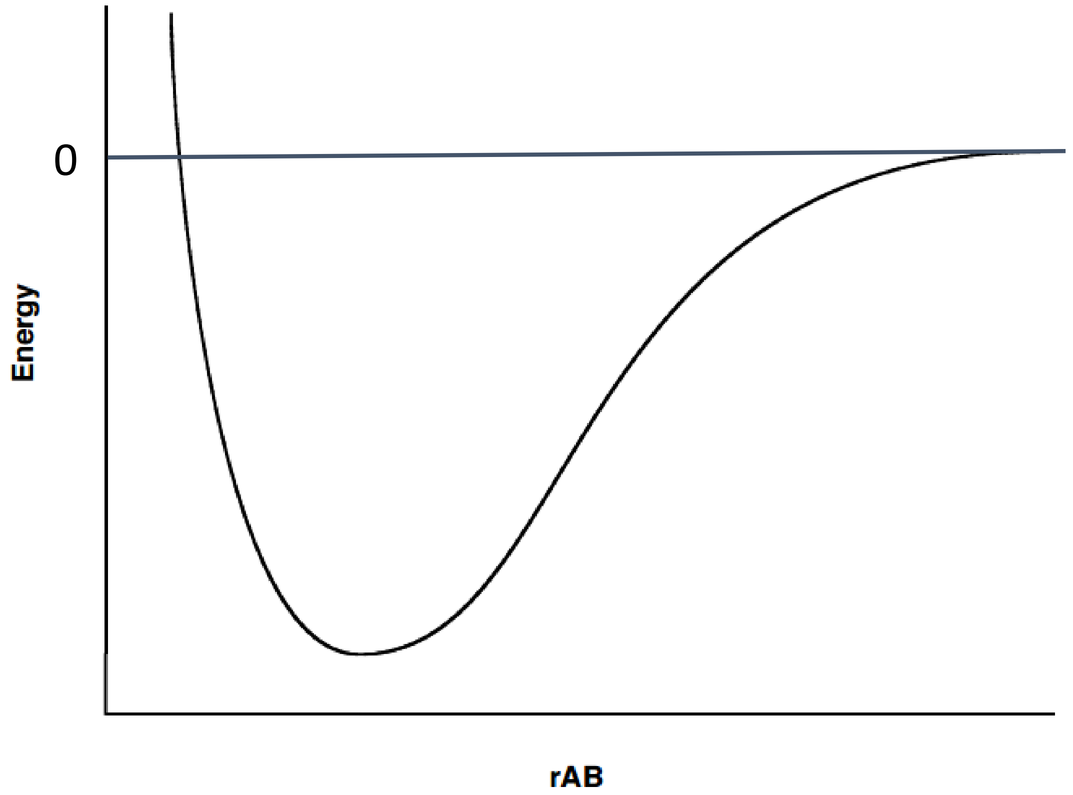
Electronic Equation for 2 electron system in SI units

$$\hat{H} = \underbrace{\frac{-\hbar^2}{2M}\nabla_1^2 - \frac{-\hbar^2}{2M}\nabla_2^2}_{\hat{T}_e} \underbrace{- \frac{Ze^2}{4\pi\varepsilon_0 r_1} - \frac{Ze^2}{4\pi\varepsilon_0 r_2}}_{\hat{V}_{Ne}} \underbrace{+ \frac{e^2}{4\pi\varepsilon_0 |r_1 - r_2|}}_{\hat{V}_{ee}}$$

Electronic Equation for N electron system in SI units

$$\hat{H}\Psi = \hat{E}\Psi = \sum_{i=1}^{N}\left(\frac{-\hbar^2}{2M}\nabla_i^2\Psi - Ze^2\sum_{R}\frac{1}{|r_i - R|}\Psi\right) + \frac{1}{2}\sum_{i\neq j}\frac{e^2}{|r_i - r_j|}\Psi$$

One-dimensional PES



Standard Diatomic Bond Stretch

- Diatomic bond stretching has only one degree of freedom
- Each structure is associated with a unique energy
- A PES displays the energy of a molecule as a function of its geometry
- PES depends on the relative location of the atoms not the absolute

Two-dimensional PES

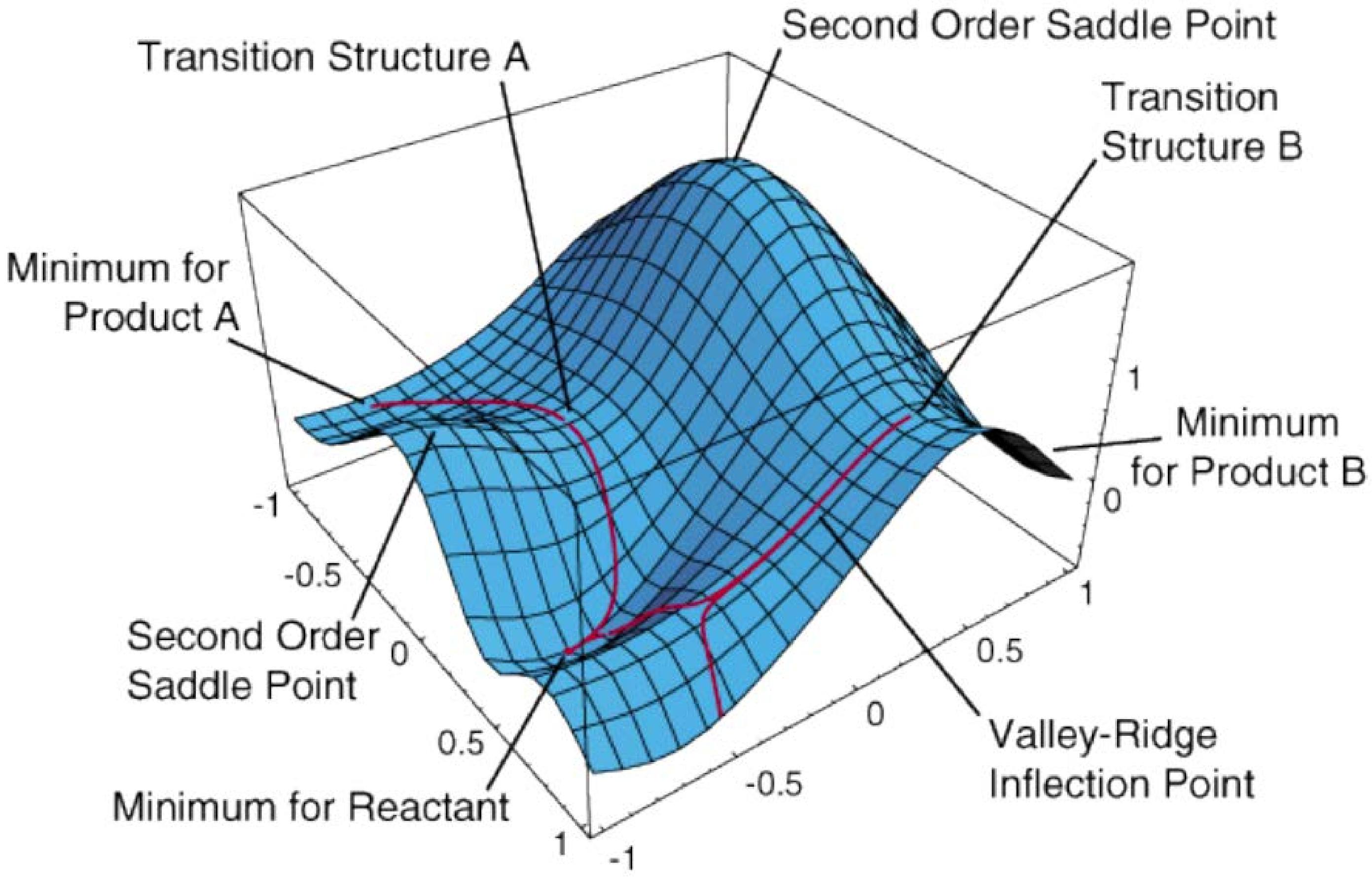
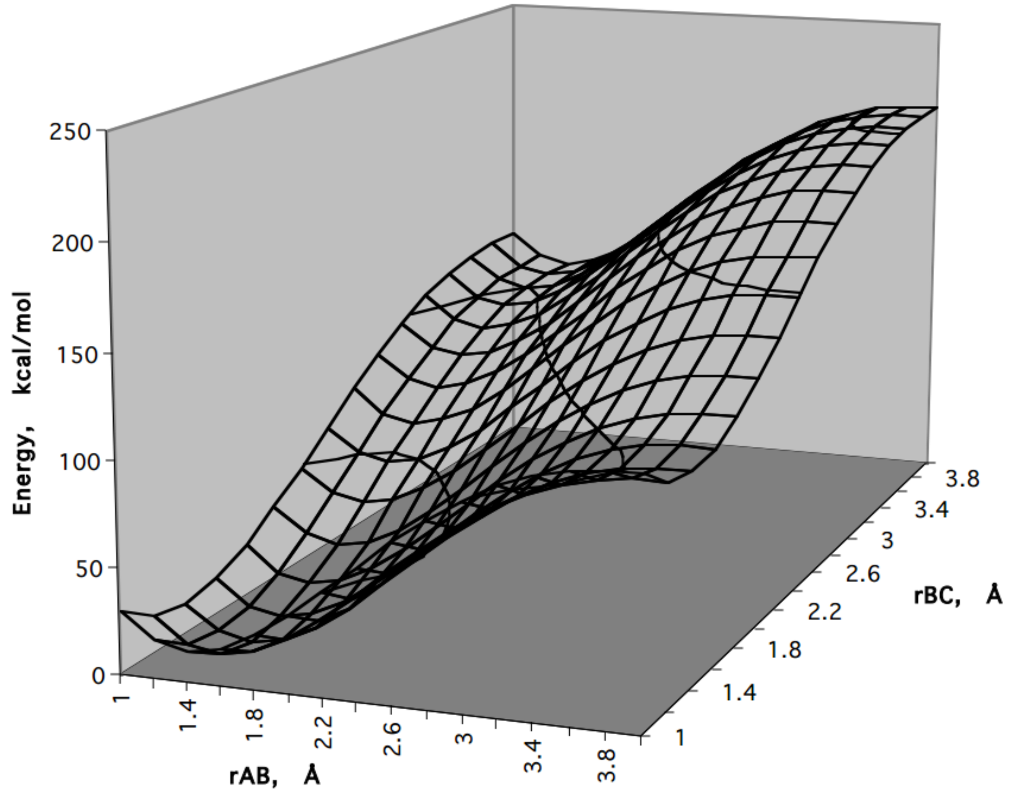
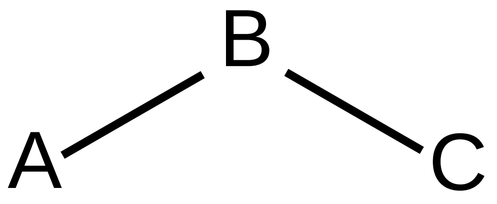


Image Credit: Prof. H.B. Schlegel, Wayne State University

Two-dimensional PES Cont.





- Based upon 3N-6 (non-linear) degrees of freedom
  - 6 correlates to the translation and rotational movement
- More that 2-dimensions don't graph well. Generally a PES is displayed as a 2D slice of the entire energy surface
- In this example the bond angle between ABC is being held constant, while the bond length are varied

Image Credit: Essentials of Computational Chemistry: Theories and Models, 2nd Ed. by Prof. C. J. Cramer

Two-dimensional PES Cont.

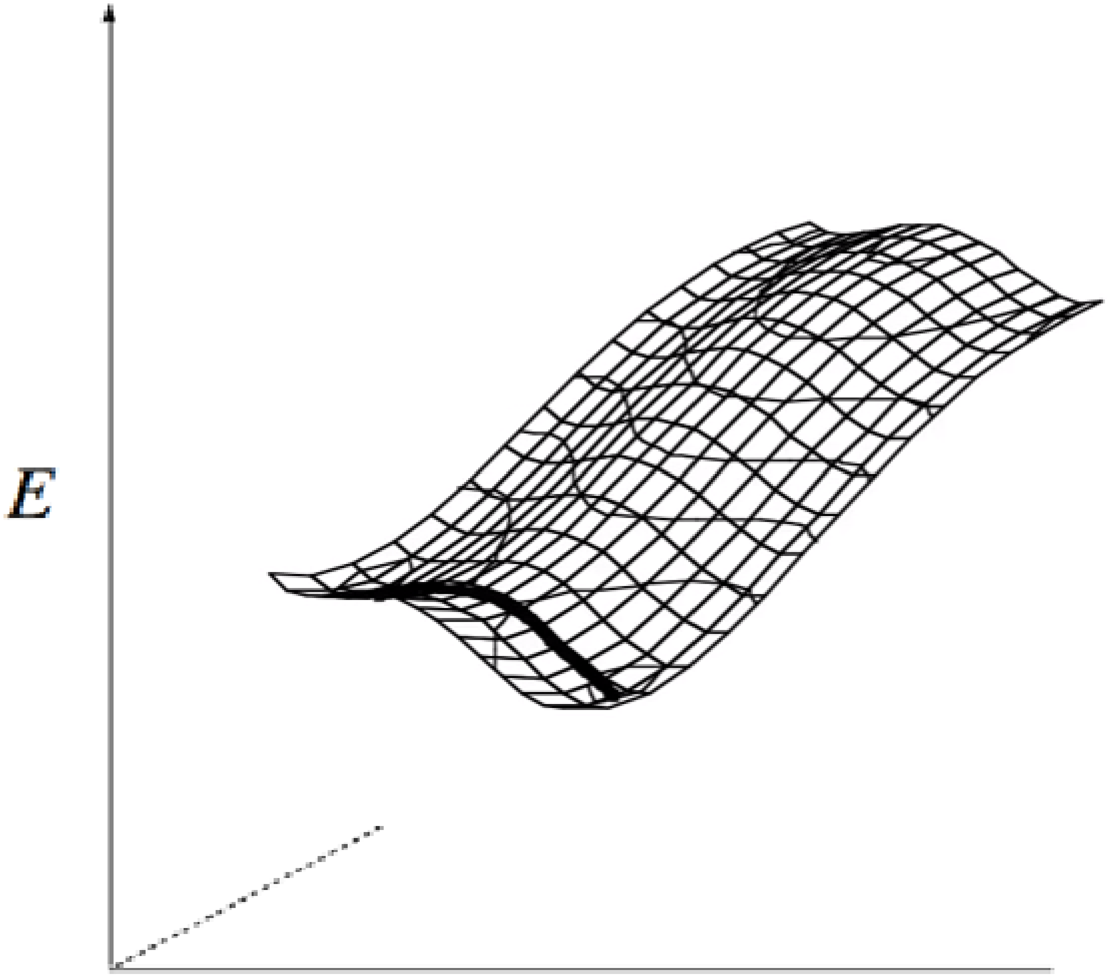


Image Credit: Prof. C. J. Cramer, University of Minnesota

- The PES can be used to obtain useful chemical information
- Using two minimums on the surface, the equilibrium constant between the points can be calculated

$$K = e^{-\Delta G/RT}$$

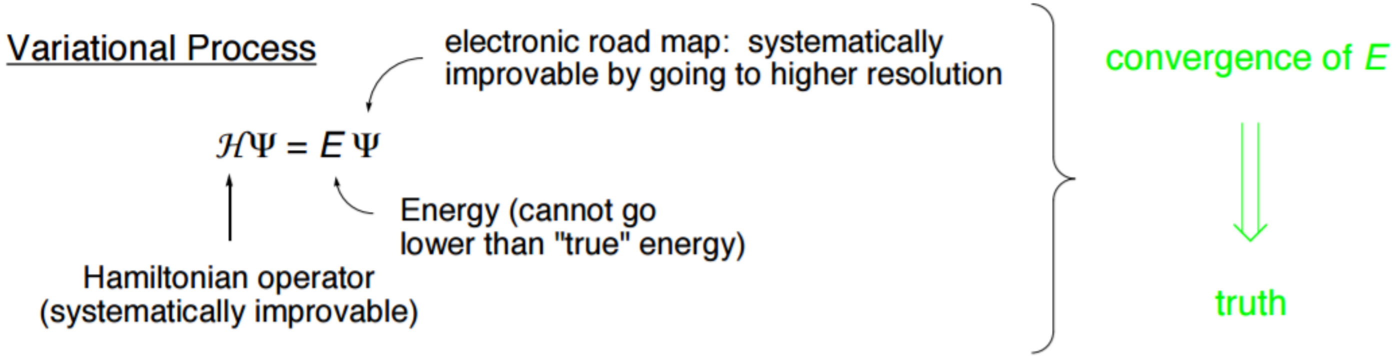
- The an approximate rate constant for a minimum traveling through a transition state can be calculated

$$k = \frac{k_B T}{h} e^{-\Delta G^{\ddagger}/RT}$$

The Variational principle for ground state

- In quantum mechanics, one often encounters systems for which the Schrödinger equation cannot be solved exactly
- There are two methods to approximately solve the Schrödinger equation:
    - Perturbation Theory
    - Variational Theorem

$$\langle E\rangle = E_{Trial} = \frac{\langle\Psi|H|\Psi\rangle}{\langle\Psi|\Psi\rangle} = \frac{\int \Psi^{*} H\Psi d\tau}{\int \Psi^{*}\Psi d\tau} \geq E_0$$



Variational Process

electronic road map: systematically improvable by going to higher resolution

$\mathcal{H}\Psi = E\,\Psi$

Energy (cannot go lower than "true" energy)

Hamiltonian operator (systematically improvable)

convergence of *E*

truth

Diagram Credit: Prof. C. J. Cramer, University of Minnesota

Hartree-Fock (HF)

Wave function for ground-state Helium ($1s^2$)

$$\psi = \frac{1}{\sqrt{2}}\left[\varphi_{1s}(\vec{r}_1)\alpha_1\varphi_{1s}(\vec{r}_2)\beta_2 - \varphi_{1s}(\vec{r}_1)\beta_1\varphi_{1s}(\vec{r}_2)\alpha_2\right] \quad \text{or} \quad \psi = \frac{1}{\sqrt{2}}\left[1s(1)\alpha_1 1s(2)\beta_2 - 1s(1)\beta_1 1s(2)\alpha_2\right]$$

$$\Psi_0 \approx \Psi_{HF} = \frac{1}{\sqrt{N!}}\begin{vmatrix} \psi_1(\vec{x}_1) & \psi_2(\vec{x}_1) & \dots & \psi_N(\vec{x}_1) \\ \psi_1(\vec{x}_2) & \psi_2(\vec{x}_2) & \dots & \psi_N(\vec{x}_2) \\ \vdots & \vdots & & \vdots \\ \psi_1(\vec{x}_N) & \psi_2(\vec{x}_N) & \dots & \psi_N(\vec{x}_N) \end{vmatrix}$$

Wave function for ground-state Helium ($1s^2$) can be written as 2x2 determinant called as slater determinant

$$\psi(1,2) = \frac{1}{\sqrt{2}}\begin{vmatrix} 1s(1)\alpha_1 & 1s(1)\beta_1 \\ 1s(2)\alpha_2 & 1s(2)\beta_2 \end{vmatrix} = \frac{1}{\sqrt{2}}\left[1s(1)\alpha_1 1s(2)\beta_2 - 1s(1)\beta_1 1s(2)\alpha_2\right] \qquad \Psi(1,2) = -\Psi(2,1)$$

Different spin orbitals (combo of spatial and spin part of an orbital taken together) are put in different columns different electrons are put in different rows

A Slater determinant is automatically antisymmetric wrt the exchange of two electrons

Hartree-Fock (HF)

- Hartree’s original method neglected to consider that the wave function in a multi-electron atom (or molecule) must be antisymmetric with respect to electron exchange.

$$E_H = \sum_{i=1}^{N} \varepsilon_i - \sum_{i=1}^{N} \sum_{j>1} J_{ij} \qquad \varepsilon_i \equiv \int \varphi_i(\tau) \left(-\frac{1}{2} \nabla^2 - V_{ext}(\tau) \right) \varphi_i(\tau) \delta\tau$$

ε_i = Energy of an electron

- The Hartree-Fock is an extension, using antisymmetrized wave functions.

- Resulting in additional “Exchange” terms in the Effective Hamiltonians and “Exchange Integrals” in the expression for the energy.

$$J_{ij} = \left\langle \varphi_i \varphi_j \left| \frac{1}{r_{12}} \right| \varphi_i \varphi_j \right\rangle = \int_{\vec{r}_1} \int_{\vec{r}_2} \frac{\left[\varphi_i^*(\vec{r}_1) \varphi_i(\vec{r}_1) \right] \left[\varphi_j^*(\vec{r}_2) \varphi_j(\vec{r}_2) \right]}{r_{12}} d\vec{r}_1 d\vec{r}_2$$

Coulomb Integral

$$E_{HF} = \sum_{i=1}^{N} \varepsilon_i - \sum_{i=1}^{N} \sum_{j>1} (2J_{ij} - K_{ij})$$

$$K_{ij} = \left\langle \varphi_i \varphi_j \left| \frac{1}{r_{12}} \right| \varphi_j \varphi_i \right\rangle = \int_{\vec{r}_1} \int_{\vec{r}_2} \frac{\left[\varphi_i^*(\vec{r}_1) \varphi_j(\vec{r}_1) \right] \left[\varphi_j^*(\vec{r}_2) \varphi_i(\vec{r}_2) \right]}{r_{12}} d\vec{r}_1 d\vec{r}_2$$

Exchange Integral

Continue with wavefunction theory

- Ψ is complicated
- Difficult to interpret
- Has a strange unit (prob. density)$^{1/2}$
- Can we use a physical observable?
- Which particular physical observable is useful?
- Physical observable that allows us to construct the Hamiltonian

Thomas-Fermi-Dirac Model (TFD)

- Conventional approach of using Ψ cannot be probed experimentally and it depends on 4N (x, y, z and spin) variable where N being number of electron.

- Thomas-Fermi were the first to use electron density (ρ) as a physical observable to calculate the Hamiltonian (with no reference to Ψ)

- ρ is define as a function of three spatial coordinates:

$$\rho \equiv \rho(\tau) = \rho(x, y, z)$$

- TF theory defines the kinetic and potential energy terms as functionals of ρ

$$\hat{E}_{TF}[\rho] = \hat{T}_{TF}[\rho] + \hat{E}_{Ne}[\rho] + \hat{J}[\rho]$$

- To determine the correct density, Thomas-Fermi employed a variational principle – Assuming the ground state of the system is connected to ρ for which the energy is minimized under the constraint of

$$N = \int \rho \, \delta\tau$$

Thomas-Fermi-Dirac Model (TFD)

- Based on the uniform electron gas (ueg) they propose the following functional for KE (T_{TF})

$$\hat{T}_{TF}[\rho] = C_f \int \rho^{5/3} \delta\tau \qquad C_f = \frac{3}{10}(3\pi^2)^{2/3}$$

- The energy of an atom is finally obtained using the classical expression for the nuclear-electron potential (E_{Ne}) and electron-electron potential (J).

$$\hat{E}_{Ne}[\rho] = \sum_A Z_A \int \frac{\rho}{r_a} \delta\tau \qquad \hat{J}[\rho] = \int \frac{\rho(1)\rho(2)}{r_{12}} \delta\tau_1 \delta\tau_2$$

- TF equation together with an assumed variational principle represents the first density functional theory (1927)

- Dirac introduced the exchange term $E_x[\rho]$ or $K_D[\rho]$ in (1930)

$$\hat{K}_D[\rho] = -C_x \int \rho^{4/3} \delta\tau$$

$$\hat{E}_{TF}[\rho] = \hat{T}_{TF}[\rho] + \hat{E}_{Ne}[\rho] + \hat{J}[\rho] + \hat{K}_D[\rho]$$

$$C_x = \frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}$$

Thomas-Fermi-Dirac Model (TFD)

- A further correction that was applied to the model by introducing Hole Function (h)
- The Hole function corrects the energetics error in the $\hat{J}[\rho]$ functional introduced by assuming a classical behavior

$$\left\langle \Psi \left| \sum_{i<j}^{N} \frac{1}{r_{ij}} \right| \Psi \right\rangle = \frac{1}{2} \int \int \frac{\rho(r_1)\rho(r_2)}{|r_1 - r_2|} dr_1 dr_2 + \frac{1}{2} \int \int \frac{\rho(r_1)h(r_1;r_2)}{|r_1 - r_2|} dr_1 dr_2$$

- Slater in 1951 attempted to improve the electron exchange term defined by Dirac in 1930.

- By using α=1, while Dirac used α=2/3 for the same expression

$$\hat{E}_X[\rho] = -C_x \int \rho^{4/3} \delta\tau \qquad C_x = \frac{9\alpha}{8}\left(\frac{3}{\pi}\right)^{1/3}$$

Xa (Hartree-Fock-Slater (HFS Model))

- Help improve computational costs for HF calculations
- Hartree-Fock calculations employing Slater’s exchange equation
- α has been used as an empirical value, and through empirical analysis in a variety of systems suggests that α=3/4 produces more accurate results than both α=1 and α=2/3

$$\hat{E}_X[\rho] = -C_x \int \rho^{4/3} \delta\tau \qquad C_x = \frac{9\alpha}{8}\left(\frac{3}{\pi}\right)^{1/3}$$

Hohenberg-Kohn

- In 1964 Hohenberg and Kohn proved two theorems which established DFT as a rigorous quantum chemical methodology

  The first theorem demonstrates that ρ uniquely determines the Hamiltonian and thus all the properties of the system.

- Electrons interact with one another and with an external potential

  External potential is the attraction to the nuclei

- Hohenberg and Kohn demonstrated that:
  - The ground electronic energy is determined completely by ρ
  - The ρ determines the external potential (v)
  - The Hamiltonian is determined by v

Hohenberg-Kohn Theorem I

$$E_{0,a} < \langle \Psi_{0,b} | H_a | \Psi_{0,b} \rangle$$

$$E_{0,a} < \langle \Psi_{0,b} | H_a - H_b + H_b | \Psi_{0,b} \rangle$$

$$E_{0,a} < \langle \Psi_{0,b} | H_a - H_b | \Psi_{0,b} \rangle + \langle \Psi_{0,b} | H_b | \Psi_{0,b} \rangle$$

$$E_{0,a} < \langle \Psi_{0,b} | H_a - H_b | \Psi_{0,b} \rangle + E_{0,b}$$

$$E_{0,a} < \int [v_a - v_b] \rho_0 \delta\tau + E_{0,b}$$

Assume: Two different external potentials can be consistent with the same non-degenerate ground-state density (ρ_0).

External potentials:

v_a and v_b

Potentials determine Hamiltonians:

H_a and H_b

Associate a ground-state wave function (Ψ_0) and eigenvalue (E_0)

Hohenberg-Kohn Theorem I

$$E_{0,b} < \int [v_b - v_a]\rho_0 \delta\tau + E_{0,a}$$

$$E_{0,a} + \ E_{0,b} < \int [v_b - v_a]\rho_0 \delta\tau + \int [v_a - v_b]\rho_0 \delta\tau + E_{0,b} + E_{0,a} < E_{0,b} + E_{0,a}$$

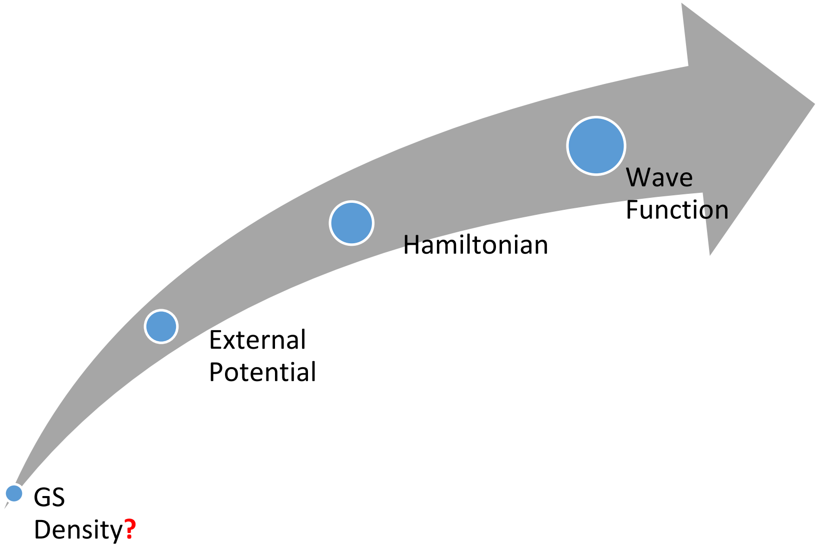
$$E_{0,a} + \ E_{0,b} < E_{0,b} + E_{0,a}$$

By assuming ρ_0 associated with Ψ_a and Ψ_b are the same permits us to eliminate the integrals as must sum to zero

The initial assumption is incorrect

Hohenberg-Kohn Theorem II

- While Theorem I proves the relationship between ρ & Ψ
- How do you get the density of a system?
- The density can be obtained through the variational principle
- Theorem II states that ρ obeys the variational principle
- From theorem I was used to get the density that determines a candidate wave function
- The candidate wave function can be used to obtain the energy expectation value



$$E_0 \leq E_{Cand} = \langle \Psi_{Cand} | H_{Cand} | \Psi_{Cand} \rangle$$

References

- Cramer, C. J. Essentials of Computational Chemistry: Theories and Models, 2nd Ed. John Wiley & Sons, Ltd. West Sussex, England 596.
- Jensen, F. Introduction to Computational Chemistry, 2nd Ed. John Wiley & Sons, Ltd. West Sussex, England 599
- Notes from Dr. Cisneros (Chem 5660) & Dr. Schwartz (Chem 5210)
- Presentation “Introduction to Density Functional Theory” by Dr. Cuevas

Thank you!