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The Born-Oppenheimer Approximation - 4.2.3

This approximation makes it possible to separate the motion of the nuclei (neutrons & protons) from the motion of the electrons. The nucleons are $\sim 1800\times$ larger than electrons, so this approximation takes into account the nucleus moving slower than electrons.

Electronic Schrödinger equation

$$\begin{array}{c}
 \begin{array}{ccc}
 \text{nuclear-nuclear} & \text{electronic} & \text{electronic} \\
 \text{repulsion} & \text{coordinates} & \text{energy} \\
 \downarrow & \downarrow & \downarrow
 \end{array} \\
 (H_{el} + V_N) \Psi_{el}(g_i; g_k) = E_{el} \Psi_{el}(g_i; g_k) \\
 \downarrow \qquad \qquad \qquad \downarrow \qquad \qquad \qquad \downarrow \\
 -\sum_i \frac{\hbar^2}{2m_e} + \sum_i \sum_k \frac{e^2 Z_k}{r_{ik}} + \sum_{i,j} \frac{e^2}{r_{ij}} \qquad \downarrow \\
 \qquad \qquad \qquad \qquad \qquad \qquad \text{nuclear} \\
 \qquad \qquad \qquad \qquad \qquad \qquad \text{coordinates} \\
 \qquad \qquad \qquad \qquad \qquad \qquad \text{parameters}
 \end{array}$$

★ The Secular Equation - 4.3.2

We want to ~~find~~ find the best one-electron wavefunction for a molecular system. We first want to select N basis functions, then find N^2 values for H_{ij} and S_{ij} . ~~then form~~ then form the secular determinant to find N roots E_j of the equation. Then lastly, for all of the N values of E_j , solve the set of linear equations to find the basis set coefficients a_{ij} for the orbital.

$$\begin{array}{c}
 \begin{array}{ccc}
 \text{unknown} & & \text{overlap integral} \\
 \text{coefficients} & & \downarrow \\
 \sum_{i=1}^N a_i (H_{ki} - E S_{ki}) = 0 & \text{V/S} & \uparrow \\
 \uparrow & & \uparrow \text{All values of } k \\
 \text{resonance} & & \\
 \text{integral} & &
 \end{array}
 \end{array}$$

★ 4.5.1. Hartree-product Wave Functions

The approximation ~~takes into account~~ ^{involves using} a ~~single~~ one-electron model of a Hamiltonian. ~~Use~~ In a multi-electron system, ^{the electrons are} multiplied to each other to resemble a wavefunction for a multi-electron system.

$$(4.35) \quad \psi_{HP} = \psi_1 \psi_2 \dots \psi_N$$

In short, the energy of the ψ_{HP} is the sum of the one electron values. Does not take into account attraction / repulsion forces ~~at all~~.

★ 4.5.2 The Hartree Hamiltonian

This approximation uses the ideas of the Hartree-product wave function but takes into account electron-electron interactions. Equation (4.39) is a ~~more~~ better approximation than (4.35) in the text.

$$E = \sum_i \epsilon_i - \frac{1}{2} \sum_{i \neq j} \iint \frac{|\psi_i|^2 |\psi_j|^2}{r_{ij}} dr_i dr_j$$

$|\psi|^2$ is the ^{charge} probability density. $i \neq j$ are electrons

★ 4.5.3 Electron Spin & Antisymmetry

This approximation deals with involving spin eigenfunctions. It uses the spin quantum number, ~~and also involves~~ which tells us

↳ no two electrons uses the same quantum number.

In different
orbitals w/
the same
spin

These principles provides the basis for what we know as the Pauli ~~ex~~ exclusion principle. So when taking into account spin, we use (4.43) to satisfy the Pauli ~~ex~~ exclusion principle.

$$^3\psi_{sp} = \frac{1}{\sqrt{2}} [\overset{\text{electron 1}}{\psi_a(1)} \overset{\text{electron 2}}{\alpha(1)} \psi_b(2) \alpha(2) - \psi_a(2) \alpha(2) \psi_b(1) \alpha(1)]$$

α is ~~electron~~ the spin

★ 4.5.4 Slater Determinants

The Slater Determinant takes into account ~~when~~ the wavefunction when you have electrons ~~with different spins~~ ^{with different spins} in ~~an energy level~~ having different spins in an energy orbital. ~~in~~ (4.50) differs ~~from~~ from (4.43) for this reason. ~~When you integrate each wave function, you are able to solve for the loss of variable Kab, the Coulomb repulsion. We find this to be less than for the approximation above because electrons of the same spin repel each other more than electrons of different spin.~~

$$\psi_{sp} = \frac{1}{\sqrt{2}} [\psi_a(1) \alpha(1) \psi_b(2) \beta(2) - \psi_a(2) \alpha(2) \psi_b(1) \beta(1)]$$

α & β \rightarrow different spins

* 4.5.5 The Hartree-Fock Self-consistent Field Method

This approximation takes into account the ~~interaction~~ interaction of electrons, including the exchange effects of Coulomb repulsion. Its main drawback is its one-electron nature and other electron interactions. It is still flawed in its approximation but it provides a stepping stone until we have a better approximation to solve the Schrödinger equation.

Flow Chart of HF SCF procedure

↑
that's good
main idea

One electron

$$P_i = -\frac{1}{2} \nabla_i^2 - \sum_k \frac{Z_k}{r_{ik}}$$

$2J_i - K_i$, where $J_i + K_i$ are operators

$$+ V_i \left\{ \begin{matrix} \text{HF} \\ \psi_i \end{matrix} \right\}$$