Lecture 14: The Electronic Schrödinger Equation

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Mulliken's Legacy

I feel that chemical binding has not one nature, but many. Also, I do not wish to be necessarily committed to the familiar concept that molecules are composed of atoms, in other words, that atoms are still atoms when they have formed molecules.

A molecule is a molecule is a molecule.

- First principles / *ab initio* quantum chemistry must start from electrons and nuclei, not atoms

The Electronic Hamiltonian

$$\hat{H}_{\mathrm{e}} = \hat{T}_{\mathrm{e}} + \hat{V}_{\mathrm{ee}} + \hat{V}_{\mathrm{en}} + \hat{V}_{\mathrm{nn}}$$

- $\hat{T}$: kinetic, $\hat{V}$: potential energy operators
- e: electron, n: nucleus
- N_{e} electrons, N_{n} nuclei
- Many body, but contains at most pair terms
- No empirical parameters

Kinetic Energy

- Kinetic energy operator of the electrons (atomic units):

$$\hat{T}_\mathrm{e} = \sum_{i=1}^{N_\mathrm{e}} \frac{\hat{\mathbf{p}}_i^2}{2m_\mathrm{e}}$$

- Recap: Momentum operator for one particle:

$$\hat{\mathbf{p}} = \frac{1}{i}\nabla$$

- The nuclear kinetic energy is (initially) neglected, because nuclei are much heavier than electrons: Born-Oppenheimer (BO) or "clamped nuclei" approximation

Potential Energy

- Operator of electron-electron repulsion:

$$\hat{V}_{\mathrm{ee}} = \frac{1}{2} \sum_{\substack{i,j=1 \\ i \neq j}}^{N_{\mathrm{e}}} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

- Operator of electron-nucleus attraction:

$$\hat{V}_{\mathrm{en}} = -\sum_{i=1}^{N_{\mathrm{e}}} \sum_{I=1}^{N_{\mathrm{n}}} \frac{Z_I}{|\mathbf{r}_i - \mathbf{r}_I|}$$

- Operator of nucleus-nucleus repulsion:

$$\hat{V}_{\mathrm{ee}} = \frac{1}{2} \sum_{\substack{IJ=1 \\ I \neq J}}^{N_{\mathrm{n}}} \frac{Z_I Z_J}{|\mathbf{r}_I - \mathbf{r}_J|}$$

Stationary Molecular Schrödinger Equation

$$\hat{H}_{\mathrm{e}}\Psi_n = E_n\Psi_n$$

- Solution: All possible electronic energy levels and states
- The energies (and wavefunctions) depend parametrically on the nuclear positions: BO energy surfaces
- Note $\Psi_n = \Psi_n(x_1, \ldots, x_n)$ is generally not separable; $x = (\mathbf{r}, \sigma)$: spin-space coordinates of one electron
- May be solved exactly, but Hilbert space dimension grows factorially with number of electrons
- "Quantum many-body problem"

Spin-Statistics Theorem ("6. Postulate")

The wavefunction of N identical particles of a (half) integer spin transforms according to the totally (anti-) symmetric IRREP of the symmetric group $S(N)$.

- Corollary: Many-electron states are antisymmetric under exchange of any two electrons (implies Pauli principle)