Elementary Wave Mechanics

Density-Functional Theory of Atoms and Molecules
– Robert G. Parr and Weitao Yang

Chapter 1

The Schrödinger equation

Any problem in the electronic structure of matter is covered by Schrödinger's equation including the time. In most cases, however, one is concerned with atoms and molecules without time-dependent interactions, so we may focus on the time-independent Schrodinger equation. For an isolated N-electron atomic or molecular system in the Born-Oppenheimer nonrelativistic approximation, this is given by

$$\hat{H}\Psi = E\Psi$$

where E is the electronic energy, $\Psi = \Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_n)$ is the wave function, and $\hat{H}$ is the Hamiltonian operator,

$$\hat{H} = \sum_{i=1}^{N} \left(-\tfrac{1}{2}\nabla_i^2\right) + \sum_{i=1}^{N} v(\mathbf{r}_i) + \sum_{i<j}^{N} \frac{1}{r_{ij}}$$

The Schrödinger equation

$$\hat{H} = \sum_{i=1}^{N} \left(-\tfrac{1}{2}\nabla_i^2\right) + \sum_{i=1}^{N} v(\mathbf{r}_i) + \sum_{i<j} \frac{1}{r_{ij}}$$

in which

$$v(\mathbf{r}_i) = -\sum_{\alpha} \frac{Z_\alpha}{r_{i\alpha}}$$

is the "external" potential acting on electron i, the potential due to nuclei of charges Z_α. The coordinates $\mathbf{x}_i$ of electron i comprise space coordinates $\mathbf{r}_i$ and spin coordinates s_i. Atomic units are employed here and throughout this book (unless otherwise specified): the length unit is the Bohr radius $a_0 (=0.5292\ \text{Å})$, the charge unit is the charge of the electron, e, and the mass unit is the mass of the electron, m_e.

The Hamiltonian operator

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

where

$$\hat{T} = \sum_{i=1}^{N} \left(-\tfrac{1}{2}\nabla_i^2\right)$$

is the kinetic energy operator,

$$\hat{V}_{ne} = \sum_{i=1}^{N} v(r_i)$$

is the electron–nucleus attraction energy operator, and

$$\hat{V}_{ee} = \sum_{i<j}^{N} \frac{1}{r_{ij}}$$

is the electron–electron repulsion energy operator.

The total energy

$$V_{nn} = \sum_{\alpha < \beta} \frac{Z_\alpha Z_\beta}{R_{\alpha\beta}}$$

$$W = E + V_{nn}$$

Probability distribution function

$$|\Psi(\mathbf{r}^N, s^N)|^2 \, dr^N = \text{probability of finding the system}$$

with position coordinates between $\mathbf{r}^N$ and $\mathbf{r}^N + d\mathbf{r}^N$ and spin coordinates equal to s^N

Here $d\mathbf{r}^N = d\mathbf{r}_1, d\mathbf{r}_2, \ldots, d\mathbf{r}_N$; $\mathbf{r}^N$ stands for the set $\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N$, and s^N stands for the set $s_1, s_2, \ldots, s_N$. The spatial coordinates are continuous, while the spin coordinates are discrete. Because electrons are fermions, Ψ also must be antisymmetric with respect to interchange of the coordinates (both space and spin) of any two electrons.

$$\int \Psi_k^* \Psi_l \, d\mathbf{x}^N = \langle \Psi_k \mid \Psi_l \rangle = \delta_{kl}$$

Expectation values of observables

$$\langle \hat{A} \rangle = \frac{\int \Psi^* \hat{A} \Psi \, d\mathbf{x}}{\int \Psi^* \Psi \, d\mathbf{x}} = \frac{\langle \Psi | \hat{A} | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

$$T[\Psi] = \langle \hat{T} \rangle = \int \Psi^* \hat{T} \Psi \, d\mathbf{x}$$

$$V[\Psi] = \langle \hat{V} \rangle = \int \Psi^* \hat{V} \Psi \, d\mathbf{x}$$

$$E[\Psi] = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

Variational principle for the ground state

$$E[\Psi] = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

The energy computed from a guessed Ψ is an upper bound to the true ground-state energy E_0. Full minimization of the functional $E[\Psi]$ with respect to all allowed N-electron wave functions will give the true ground state Ψ_0 and energy $E[\Psi_0] = E_0$; that is,

$$E_0 = \min_{\Psi} E[\Psi]$$

The Hartree-Fock approximation

Suppose now that Ψ is approximated as an antisymmetrized product of N orthonormal spin orbitals $\psi_i(\mathbf{x})$, each a product of a spatial orbital $\phi_k(\mathbf{r})$ and a spin function $\sigma(s) = \alpha(s)$ or $\beta(s)$, the *Slater determinant*

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

$$= \frac{1}{\sqrt{N!}} \det[\psi_1 \psi_2 \cdots \psi_N]$$

The Hartree-Fock approximation

The normalization integral $\langle \Psi_{HF} | \Psi_{HF} \rangle$ is equal to 1, and the energy expectation value is found to be given by the formula (for example, see Parr 1963)

$$E_{HF} = \langle \Psi_{HF} | \hat{H} | \Psi_{HF} \rangle = \sum_{i=1}^{N} H_i + \tfrac{1}{2} \sum_{i,j=1}^{N} (J_{ij} - K_{ij})$$

where

$$H_i = \int \psi_i^*(\mathbf{x})[-\tfrac{1}{2}\nabla^2 + v(\mathbf{x})] \psi_i(\mathbf{x}) \, d\mathbf{x}$$

$$J_{ij} = \iint \psi_i(\mathbf{x}_1)\psi_i^*(\mathbf{x}_1) \frac{1}{r_{12}} \psi_j^*(\mathbf{x}_2)\psi_j(\mathbf{x}_2) \, d\mathbf{x}_1 \, d\mathbf{x}_2$$

$$K_{ij} = \iint \psi_i^*(\mathbf{x}_1)\psi_j(\mathbf{x}_1) \frac{1}{r_{12}} \psi_i(\mathbf{x}_2)\psi_j^*(\mathbf{x}_2) \, d\mathbf{x}_1 \, d\mathbf{x}_2$$

The Hartree-Fock approximation

$$J_{ij} = \iint \psi_i(\mathbf{x}_1) \psi_i^*(\mathbf{x}_1) \frac{1}{r_{12}} \psi_j^*(\mathbf{x}_2) \psi_j(\mathbf{x}_2) \, d\mathbf{x}_1 \, d\mathbf{x}_2$$

$$K_{ij} = \iint \psi_i^*(\mathbf{x}_1) \psi_j(\mathbf{x}_1) \frac{1}{r_{12}} \psi_i(\mathbf{x}_2) \psi_j^*(\mathbf{x}_2) \, d\mathbf{x}_1 \, d\mathbf{x}_2$$

These integrals are all real, and $J_{ij} \geqslant K_{ij} \geqslant 0$. The J_{ij} are called *Coulomb integrals*, the K_{ij} are called *exchange integrals*. We have the important equality

$$J_{ii} = K_{ii}$$

The Hartree-Fock differential equation

$$\hat{F}\psi_i(\mathbf{x}) = \sum_{j=1}^{N} \varepsilon_{ij}\psi_j(\mathbf{x})$$

$$\varepsilon_{ji}^* = \varepsilon_{ij}$$

where

$$\hat{F} = -\tfrac{1}{2}\nabla^2 + v + \hat{g}$$

in which the Coulomb-exchange operator $\hat{g}(x_1)$ is given by

$$\hat{g} = \hat{j} - \hat{k}$$

Here

$$\hat{j}(\mathbf{x}_1)f(\mathbf{x}_1) \equiv \sum_{k=1}^{N} \int \psi_k^*(\mathbf{x}_2)\psi_k(\mathbf{x}_2)\frac{1}{r_{12}}f(\mathbf{x}_1)\,d\mathbf{x}_2$$

and

$$\hat{k}(\mathbf{x}_1)f(\mathbf{x}_1) \equiv \sum_{k=1}^{N} \int \psi_k^*(\mathbf{x}_2)f(\mathbf{x}_2)\frac{1}{r_{12}}\psi_k(\mathbf{x}_1)\,d\mathbf{x}_2$$

with $f(\mathbf{x}_1)$ an arbitrary function.

Orbital energy

$$\varepsilon_i \equiv \varepsilon_{ii} = \langle \psi_i | \, \hat{F} \, | \psi_i \rangle = H_i + \sum_{j=1}^{N} (J_{ij} - K_{ij})$$

Summing over i

$$E_{\mathrm{HF}} = \sum_{i=1}^{N} \varepsilon_i - V_{ee}$$

where the symbol V_{ee} stands for the total electron–electron repulsion energy

$$V_{ee} = \int \Psi_{\mathrm{HF}}^*(\mathbf{x}^N) \left(\sum_{i<j} \frac{1}{r_{ij}} \right) \Psi_{\mathrm{HF}}(\mathbf{x}^N) \, d\mathbf{x}^N$$

$$= \tfrac{1}{2} \sum_{i,j=1}^{N} (J_{ij} - K_{ij})$$

Total molecular energy

$$W_{\mathrm{HF}} = \sum_{i=1}^{N} \varepsilon_i - V_{ee} + V_{nn}$$

$$= \sum_{i=1}^{N} H_i + V_{ee} + V_{nn}$$

Note that neither E_{HF} nor W_{HF} is equal to the sum of orbital energies.

Restricted Hartree-Fock method (RHF)

For a system having an even number of electrons, in what is called the *restricted Hartree–Fock method* (RHF), the N orbitals ψ_i are taken to comprise $N/2$ orbitals of form $\phi_k(\mathbf{r})\alpha(s)$ and $N/2$ orbitals of form $\phi_k(\mathbf{r})\beta(s)$. The energy formula

$$E_{\mathrm{HF}} = 2 \sum_{k=1}^{N/2} H_k + \sum_{k,l=1}^{N/2} (2J_{kl} - K_{kl})$$

where

$$H_k = \int \phi_k^*(\mathbf{r})\left[-\tfrac{1}{2}\nabla^2 + v(\mathbf{r})\right]\phi_k(\mathbf{r})\,d\mathbf{r}$$

Restricted Hartree-Fock method (RHF)

$$J_{kl} = \iint |\phi_k(\mathbf{r}_1)|^2 \frac{1}{r_{12}} |\phi_l(\mathbf{r}_2)|^2 \, d\mathbf{r}_1 \, d\mathbf{r}_2$$

$$K_{kl} = \iint \phi_k^*(\mathbf{r}_1)\phi_l(\mathbf{r}_1) \frac{1}{r_{12}} \phi_k(\mathbf{r}_2)\phi_l^*(\mathbf{r}_2) \, d\mathbf{r}_1 \, d\mathbf{r}_2$$

$$\hat{F}\phi_k(\mathbf{r}) = \sum_{l=1}^{N/2} \varepsilon_{kl}\phi_l(\mathbf{r})$$

$$\hat{j}(\mathbf{r}_1)f(\mathbf{r}_1) \equiv 2 \sum_{m=1}^{N/2} \int |\phi_m(\mathbf{r}_2)|^2 \frac{1}{r_{12}} \, d\mathbf{r}_2 f(\mathbf{r}_1)$$

$$\hat{k}(\mathbf{r}_1)f(\mathbf{r}_1) \equiv \sum_{m=1}^{N/2} \int \phi_m^*(\mathbf{r}_2)f(\mathbf{r}_2) \frac{1}{r_{12}} \, d\mathbf{r}_2 \phi_m(\mathbf{r}_1)$$

Restricted Hartree-Fock method (RHF)

$$\Psi_{\text{HF}} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\mathbf{r}_1)\alpha(s_1) & \phi_1(\mathbf{r}_1)\beta(s_1) & \cdots & \phi_{N/2}(\mathbf{r}_1)\beta(s_1) \\ \phi_1(\mathbf{r}_2)\alpha(s_2) & \phi_1(\mathbf{r}_2)\beta(s_2) & \cdots & \phi_{N/2}(\mathbf{r}_2)\beta(s_2) \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ \phi_1(\mathbf{r}_N)\alpha(s_N) & \phi_1(\mathbf{r}_N)\beta(s_N) & & \phi_{N/2}(\mathbf{r}_N)\beta(s_N) \end{vmatrix}$$

$$\hat{F}\lambda_m(\mathbf{r}) = \varepsilon_m^{\lambda}\lambda_m(\mathbf{r})$$

$$\varepsilon_m^{\lambda} = -I_m$$

Canonical Hartree-Fock equations

$$\lambda_m \sim \exp\left[-(-2\varepsilon_{\max})^{1/2}r\right] \quad \text{for large } \mathbf{r}$$

Limitations of the Hartree-Fock approximation

Correlation energy

The exact wave function for a system of many interacting electrons is never a single determinant or a simple combination of a few determinants, however. The calculation of the error in energy, called *correlation energy*, here defined to be negative,

$$E_{\text{corr}}^{\text{HF}} = E - E_{\text{HF}}$$

is a major problem in many-body theory on which there has been a vast amount of work and much progress has been made.

Correlation energy

Correlation energy tends to remain constant for atomic and molecular changes that conserve the numbers and types of chemical bonds, but it can change drastically and become determinative when bonds change. Its magnitude can vary from 20 or 30 to thousands of kilocalories per mole, from a few hundredths of an atomic unit on up. Exchange energies are an order of magnitude or more bigger, even if the self-exchange term is omitted.

Electron density

In an electronic system, the number of electrons per unit volume in a given state is the *electron density* for that state. This quantity will be of great importance in this book; we designate it by $\rho(\mathbf{r})$. Its formula in terms of Ψ is

$$\rho(\mathbf{r}_1) = N \int \cdots \int |\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N)|^2 \, ds_1 \, d\mathbf{x}_2 \cdots d\mathbf{x}_N$$

This is a nonnegative simple function of three variables, x, y, and z, integrating to the total number of electrons,

$$\int \rho(\mathbf{r}) \, d\mathbf{r} = N$$

Electron density

At any atomic nucleus in an atom, molecule, or solid, the electron density has a finite value; for an atom we designate this $\rho(0)$. In the neighborhood of a nucleus there always is a cusp in the density owing to the necessity for Hamiltonian terms $-\frac{1}{2}\nabla^2 - (Z_\alpha/r_\alpha)$ not to cause blowups in $\hat{H}\Psi$ there. The specific cusp condition is (for example, see Davidson

$$\frac{\partial}{\partial r_\alpha}\bar{\rho}(r_\alpha)\Big|_{r_\alpha=0} = -2Z_\alpha\bar{\rho}(0)$$

where $\bar{\rho}(r_\alpha)$ is the spherical average of $\rho(r_\alpha)$.

Electron density

Another important result is the long-range law for electron density,

$$\rho \sim \exp\left[-2(2I_{\min})^{1/2}r\right] \qquad (1.5.4)$$

where $I_{\min}$ is the exact first ionization potential (Morrell, Parr, and Levy 1975; this paper also contains a generalization of Koopmans' theorem). The corresponding Hartree–Fock result will be, from (1.3.33),

$$\rho_{\mathrm{HF}} \sim \exp\left[-2(-2\varepsilon_{\max})^{1/2}r\right] \qquad (1.5.5)$$

where $\varepsilon_{\max}$ approximates $I_{\min}$ by (1.3.32).