

Advanced Quantum Mechanics & Spectroscopy (CHEM 7520)

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Week 7-8: Advanced electronic structure theory

I. THE ELECTRONIC SCHRÖDINGER EQUATION

1) Previously we discussed how to solve the Schrödinger equation for the internal nuclear (rotational and vibrational) motion. We now turn our attention to the solution of the electronic Schrödinger equation. We will work in the molecule-fixed coordinate system, just like we did during the discussion of the vibrational motion. Although we were able to obtain a great deal of insight from the classical mechanical description of the nuclear motion, we cannot treat electrons as classical particles. In fact, according to classical mechanics, all atoms and molecules are unstable and should not exist!

2) We recall that the total energy of the molecule can be written as

$$E = \langle \Psi | \hat{H} | \Psi \rangle \quad (1)$$

where the **total molecular wavefunction** $|\Psi\rangle$ is normalized ($\langle \Psi | \Psi \rangle = 1$) and the **total molecular Hamiltonian** is defined (in atomic units) as

$$\begin{aligned} \hat{H} = & -\frac{1}{2} \sum_i^n \nabla_i^2 - \frac{1}{2} \sum_A^N \frac{1}{M_A} \nabla_A^2 \\ & - \sum_i^n \sum_A^N \frac{Z_A}{r_{iA}} + \sum_{i>j}^n \frac{1}{r_{ij}} + \sum_{A>B}^N \frac{Z_A Z_B}{R_{AB}} \end{aligned} \quad (2)$$

Here, the indices i run over the total number of electrons (n), indices A, B run over the total number of nuclei (N), M_A is the mass of the nucleus A , Z_A is the nuclear charge, R_{AB} is the distance between two nuclei, r_{iA} is the electron-nuclear distance, and r_{ij} is the distance between two electrons. The first two terms of Eq. (2) describe the **kinetic energy of the electrons and nuclei**, while the last three terms describe the **potential energy of the electron-nuclear, electron-electron, and nuclear-nuclear interaction**.

3) Within the Born-Oppenheimer approximation, the second term of Eq. (2) (the kinetic energy of the nuclei) can be neglected and the last term of Eq. (2) (the

internuclear repulsion) can be considered to be constant. The energy expression takes the form:

$$E = E_{elec} + E_{nuc} = \langle \Psi_{elec} | \hat{H}_{elec} | \Psi_{elec} \rangle + \sum_{A>B}^N \frac{Z_A Z_B}{R_{AB}} \quad (3)$$

The first term on the r.h.s. of Eq. (3) is the solution of the **electronic Schrödinger equation**

$$\hat{H}_{elec} | \Psi_{elec} \rangle = E_{elec} | \Psi_{elec} \rangle \quad (4)$$

where $| \Psi_{elec} \rangle$ is the **electronic wavefunction** that depends on the coordinates of all electrons and (parametrically) on the positions of all nuclei. The **electronic Hamiltonian** is defined as:

$$\begin{aligned} \hat{H}_{elec} &= -\frac{1}{2} \sum_i^n \nabla_i^2 - \sum_i^n \sum_A^N \frac{Z_A}{r_{iA}} + \sum_{i>j}^n \frac{1}{r_{ij}} \\ &= \sum_i^n \hat{h}_i + \sum_{i>j}^n \frac{1}{r_{ij}} \end{aligned} \quad (5)$$

In Eq. (5), we defined the one-electron operator

$$\hat{h}_i = -\frac{1}{2} \nabla_i^2 - \sum_A^N \frac{Z_A}{r_{iA}} \quad (6)$$

which is often referred to as the **core Hamiltonian**. We note that the electronic Hamiltonian only depends on the *spatial* coordinates of the electrons and not the *spin* coordinates. We will return back to this later.

4) From now on, we will be concerned with the solution of the electronic Schrödinger equation and we will define $\hat{H} \equiv \hat{H}_{elec}$ and $| \Psi \rangle \equiv | \Psi_{elec} \rangle$ for brevity.

II. THE VARIATION METHOD

1) The electronic Schrödinger equation (4) yields the exact electronic ground-state energy ($E = E_0$) provided that $| \Psi \rangle$ is the exact electronic ground-state wavefunction. Let's consider an *approximate wavefunction* $| \tilde{\Psi} \rangle$. In this case, we can write the energy as an expectation value:

$$\tilde{E} = \frac{\langle \tilde{\Psi} | \hat{H} | \tilde{\Psi} \rangle}{\langle \tilde{\Psi} | \tilde{\Psi} \rangle} \quad (7)$$

We can show that the *expectation value* (7) *may approach but never be lower than the exact ground state energy* E_0 of the system:

$$\tilde{E} \geq E_0 \quad (8)$$

Eq. (8) is known as the **variational principle**. It becomes an equality if and only if $|\tilde{\Psi}\rangle$ is the exact ground-state wavefunction.

2) To prove the variational principle, we will use the fact that the Hamiltonian \hat{H} is Hermitian and, therefore, its eigenfunctions form a complete and orthonormal set of basis functions, which we will denote as $|\Phi_I\rangle$:

$$\hat{H}|\Phi_I\rangle = E_I|\Phi_I\rangle \quad (9)$$

This orthonormal set can be used to represent any wavefunction $|\tilde{\Psi}\rangle$ as a linear combination:

$$|\tilde{\Psi}\rangle = \sum_I C_I |\Phi_I\rangle \quad (10)$$

where

$$\sum_I C_I^* C_I = 1 \quad (11)$$

Then, for the expectation value (7) we obtain:

$$\tilde{E} = \sum_{IJ} C_I^* C_J \langle \Phi_I | \hat{H} | \Phi_J \rangle = \sum_I C_I^* C_I E_I \quad (12)$$

where we used the fact the the eigenfunctions $|\Phi_I\rangle$ are orthonormal. We can now subtract the exact ground-state energy from both sides of Eq. (12):

$$\tilde{E} - E_0 = \sum_I C_I^* C_I (E_I - E_0) \quad (13)$$

Note that each term in the summation on the r.h.s. of Eq. (13) is either zero or positive, since $E_I \geq E_0$. Thus, we can conclude that

$$\tilde{E} - E_0 \geq 0 \quad (14)$$

which proves that Eq. (8) is true.

3) The variational principle states that the *energy expectation value is a rigorous upper bound to the exact ground state energy. The essential problem in the variational method is to find a wavefunction, which gives the lowest possible value of*

\tilde{E} . For this purpose, the *variational condition*

$$\delta\tilde{E} = 0 \quad (15)$$

is usually employed. If the chosen wavefunction is a good approximation to the exact wavefunction, it is possible to approach the exact energy very closely by enforcing the variational condition (15). In general, the more variational parameters are included in the variational wavefunction, the closer the exact energy can be approached as these variables are optimized.

III. ORBITALS AND THE HARTREE APPROXIMATION

1) In order to solve the electronic Schrödinger equation, we need to construct approximations to the exact many-electron wavefunction $|\Psi\rangle$. A common approach to do this is to express the many-electron wavefunction in terms of the wavefunctions that depend only on the coordinates of a single electron. These single-electron (single-particle) wavefunctions are called **orbitals**.

2) To completely describe an electron, we need four coordinates: three *spatial* coordinates that define its position in space and one coordinate that defines its *spin*. We denote the spatial coordinates as a vector \mathbf{r} and the spin coordinate as a label σ . The spin coordinate can take only two values corresponding to the spin-up state (\uparrow) or the spin-down state (\downarrow). Following the usual convention, we label the spin-up state with $\sigma = \alpha$ and the spin-down state $\sigma = \beta$. The collection of spatial and spin coordinates of an electron is denoted as $\mathbf{x} = \{\mathbf{r}, \sigma\} = \{x, y, z, \sigma\}$.

3) The wavefunction of a single electron that depends on all four (spatial and spin) coordinates is called **spin-orbital**. We will denote spin-orbitals as $|\psi_i(\mathbf{x})\rangle$. A spin-orbital of an electron can be expressed as a product of two functions that depend on the spatial and spin coordinates separately:

$$|\psi(\mathbf{x})\rangle = |\phi(\mathbf{r})\rangle |\sigma\rangle \quad (16)$$

Here, $|\phi(\mathbf{r})\rangle$ is the so-called **spatial orbital** that only depends on the spatial coordinates of an electron such that $|\phi(\mathbf{r})|^2$ is the probability of finding electron at the position \mathbf{r} . The function $|\sigma\rangle$ is called the **spin function**. Since σ takes only two values, there are only two spin functions for each electron ($|\alpha\rangle$ and $|\beta\rangle$). We require functions $|\phi(\mathbf{r})\rangle$ and $|\sigma\rangle$ to form an orthonormal set:

$$\langle\phi_i(\mathbf{r})|\phi_j(\mathbf{r})\rangle = \delta_{ij} \quad (17)$$

$$\langle \alpha | \alpha \rangle = \langle \beta | \beta \rangle = 1 \quad (18)$$

$$\langle \alpha | \beta \rangle = \langle \beta | \alpha \rangle = 0 \quad (19)$$

As a result, the spin-orbitals $|\psi_i(\mathbf{x})\rangle$ are also orthonormal:

$$\langle \psi_i(\mathbf{x}) | \psi_j(\mathbf{x}) \rangle = \delta_{ij} \quad (20)$$

Note that for a given set of K spatial orbitals $\{\phi_i(\mathbf{r})\}_{i=1}^K$, there are $2K$ spin-orbitals $\{\psi_i(\mathbf{x})\}_{i=1}^{2K}$. We can relate these two sets as follows:

$$|\psi_{2i-1}(\mathbf{x})\rangle = |\phi_i(\mathbf{r})\rangle |\alpha\rangle \quad (21)$$

$$|\psi_{2i}(\mathbf{x})\rangle = |\phi_i(\mathbf{r})\rangle |\beta\rangle \quad i = 1, 2, \dots, K \quad (22)$$

If the sets of functions $|\psi_i(\mathbf{x})\rangle$ and $|\phi_i(\mathbf{r})\rangle$ were complete, then any one-electron wavefunction could be exactly represented as their linear combination.

4) We now construct a many-electron wavefunction $|\Psi\rangle$ using the single-particle wavefunctions $|\psi_i\rangle$. In the **Hartree approximation**, a N -electron wavefunction $|\Psi\rangle$ is approximated as a product of N spin-orbitals:

$$|\Psi(\mathbf{x}_1, \dots, \mathbf{x}_N)\rangle \approx \prod_i^N |\psi_i(\mathbf{x}_i)\rangle = |\psi_1(\mathbf{x}_1)\rangle |\psi_2(\mathbf{x}_2)\rangle \dots |\psi_N(\mathbf{x}_N)\rangle \quad (23)$$

From now on, we will simplify our notation for the spin-orbitals and their spatial and spin parts:

$$|\psi(\mathbf{x}_k)\rangle = |\psi(k)\rangle = |\phi(k)\rangle |\sigma(k)\rangle \quad (24)$$

5) We can use this form of $|\Psi\rangle$ to derive a general expression for the electronic energy of the Hartree approximation.

$$E = \langle \Psi | \left(\sum_i^N \hat{h}_i + \sum_{i>j}^N \frac{1}{r_{ij}} \right) | \Psi \rangle = E_{1e} + E_{2e} \quad (25)$$

For the first term, we obtain:

$$\begin{aligned} E_{1e} &= \prod_j^N \prod_k^N \sum_i^N \langle \psi_j(j) | \hat{h}_i | \psi_k(k) \rangle \\ &= \sum_i^N \int d1 \int d2 \dots \int dN \psi_1^*(1) \psi_2^*(2) \dots \psi_N^*(N) \hat{h}_i \psi_1(1) \psi_2(2) \dots \psi_N(N) \end{aligned}$$

$$= \sum_i^N \int \psi_1^*(1) \psi_1(1) d1 \dots \int \psi_i^*(i) \hat{h}_i \psi_i(i) di \dots \int \psi_N^*(N) \psi_N(N) dN \quad (26)$$

Since spin-orbitals $\psi_i(i)$ are chosen to be orthonormal, the integral above simplifies:

$$E_{1e} = \sum_i^N \int \psi_i^*(i) \hat{h}_i \psi_i(i) di = \sum_i^N \int \psi_i^*(1) \hat{h}_1 \psi_i(1) d1 = \sum_i^N \langle \psi_i | \hat{h} | \psi_i \rangle \quad (27)$$

Thus, the first term of the Hartree energy expression reduces to a sum of the **one-electron integrals** that involve spin-orbitals $|\psi_i\rangle$ and the core Hamiltonian operator \hat{h} . For the second term, we obtain:

$$\begin{aligned} E_{2e} &= \prod_j^N \prod_k^N \sum_{i>j}^N \langle \psi_j(j) | \frac{1}{r_{ij}} | \psi_k(k) \rangle \\ &= \sum_{i>j}^N \int d1 \int d2 \dots \int dN \psi_1^*(1) \psi_2^*(2) \dots \psi_N^*(N) \frac{1}{r_{ij}} \psi_1(1) \psi_2(2) \dots \psi_N(N) \\ &= \sum_{i>j}^N \int \psi_1^*(1) \psi_1(1) d1 \dots \int \int \psi_i^*(i) \psi_j^*(j) \frac{1}{r_{ij}} \psi_i(i) \psi_j(j) di dj \dots \int \psi_N^*(N) \psi_N(N) dN \\ &= \sum_{i>j}^N \int \int \psi_i^*(i) \psi_j^*(j) \frac{1}{r_{ij}} \psi_i(i) \psi_j(j) di dj \\ &= \sum_{i>j}^N \int \int \psi_i^*(1) \psi_j^*(2) \frac{1}{r_{12}} \psi_i(1) \psi_j(2) d1 d2 = \sum_{i>j}^N \langle \psi_i \psi_j | \frac{1}{r_{12}} | \psi_i \psi_j \rangle \quad (28) \end{aligned}$$

We conclude that the second term is a sum of the **two-electron integrals** that involve the electron repulsion operator $\frac{1}{r_{12}}$.

6) The total electronic energy of the Hartree approximation is:

$$E = \sum_i^N \langle \psi_i | \hat{h} | \psi_i \rangle + \sum_{i>j}^N \langle \psi_i \psi_j | \frac{1}{r_{12}} | \psi_i \psi_j \rangle = \sum_i^N \langle i | \hat{h} | i \rangle + \sum_{i>j}^N \langle ij | ij \rangle \quad (29)$$

where the first term is a sum of the kinetic and nuclear attraction energy of all electrons in a molecule while the second term is a sum of the Coulomb repulsion energy between electrons in all unique pairs of orbitals. In Eq. (29) we introduced a shorthand notation for the one- and two-electron integrals in the spin-orbital

basis:

$$\langle i|\hat{h}|j\rangle \equiv \langle \psi_i|\hat{h}|\psi_j\rangle = \int \psi_i^*(1)\hat{h}_1\psi_j(1)d1 \quad (30)$$

$$\langle ij|kl\rangle \equiv \langle \psi_i\psi_j|\frac{1}{r_{12}}|\psi_k\psi_l\rangle = \int \int \psi_i^*(1)\psi_j^*(2)\frac{1}{r_{12}}\psi_k(1)\psi_l(2)d1d2 \quad (31)$$

The integrals $\langle ij|ij\rangle$ are often referred to as **Coulomb integrals** because they describe the Coulomb repulsion energy between two electrons occupying the spin-orbitals i and j . To see this more clearly, we can express $\langle ij|ij\rangle$ in the following form:

$$\langle ij|ij\rangle = \int \int |\psi_i(1)|^2 \frac{1}{r_{12}} |\psi_j(2)|^2 d1d2 \quad (32)$$

which can be interpreted as two electron densities $|\psi_i(1)|^2$ and $|\psi_j(2)|^2$ interacting via a Coulomb potential $\frac{1}{r_{12}}$.

7) Rather than working with spin-orbitals, we can express the Hartree energy in terms of the spatial orbitals. Let's assume that the number of electrons N is even and the first N spin-orbitals are occupied. Half of the electrons will occupy the first $N/2$ spatial orbitals with spin α and the other half will occupy $N/2$ spatial orbitals with spin β . We will use the convention:

$$|\psi_{2i-1}(\mathbf{x})\rangle = |\phi_i(\mathbf{r})\rangle |\alpha\rangle \quad (33)$$

$$|\psi_{2i}(\mathbf{x})\rangle = |\phi_i(\mathbf{r})\rangle |\beta\rangle \quad i = 1, \dots, N/2 \quad (34)$$

Thus, odd spin-orbitals will have spin α and even spin-orbitals will have spin β . Using the fact that the spin functions are normalized ($\langle \sigma|\sigma\rangle = 1$), we can integrate over the spin coordinates and obtain:

$$\begin{aligned} \langle 2i|\hat{h}|2i\rangle &= \int \phi_i^*(1)\beta^*(1)\hat{h}_1\phi_i(1)\beta(1)d1 \\ &= \int \phi_i^*(1)\hat{h}_1\phi_i(1)d1 = \langle \phi_i|\hat{h}|\phi_i\rangle \end{aligned} \quad (35)$$

$$\begin{aligned} \langle 2i2j|2i2j\rangle &= \int \int \phi_i^*(1)\beta^*(1)\phi_j^*(2)\beta^*(2)\frac{1}{r_{12}}\phi_i(1)\beta(1)\phi_j(2)\beta(2)d1d2 \\ &= \langle \phi_i\phi_j|\frac{1}{r_{12}}|\phi_i\phi_j\rangle \end{aligned} \quad (36)$$

Similar equations can be obtained for odd spin-orbitals and the their odd-even

combinations in the two-electron integrals:

$$\langle (2i-1)|\hat{h}|(2i-1)\rangle = \langle \phi_i|\hat{h}|\phi_i\rangle \quad (37)$$

$$\langle (2i-1)(2j-1)|(2i-1)(2j-1)\rangle = \langle \phi_i\phi_j|\frac{1}{r_{12}}|\phi_i\phi_j\rangle \quad (38)$$

$$\langle (2i-1)2j|(2i-1)2j\rangle = \langle \phi_i\phi_j|\frac{1}{r_{12}}|\phi_i\phi_j\rangle \quad (39)$$

$$\langle 2i(2j-1)|2i(2j-1)\rangle = \langle \phi_i\phi_j|\frac{1}{r_{12}}|\phi_i\phi_j\rangle \quad (40)$$

We get for the energy:

$$\begin{aligned} E &= \sum_{i_{\text{odd}}}^N \langle i|\hat{h}|i\rangle + \sum_{i_{\text{even}}}^N \langle i|\hat{h}|i\rangle + \sum_{i_{\text{odd}} > j_{\text{odd}}}^N \langle ij|ij\rangle + \sum_{i_{\text{even}} > j_{\text{even}}}^N \langle ij|ij\rangle \\ &+ \sum_{i_{\text{odd}} > j_{\text{even}}}^N \langle ij|ij\rangle + \sum_{i_{\text{even}} > j_{\text{odd}}}^N \langle ij|ij\rangle \\ &= 2 \sum_i^{N/2} \langle \phi_i|\hat{h}|\phi_i\rangle + 4 \sum_{i>j}^{N/2} \langle \phi_i\phi_j|\frac{1}{r_{12}}|\phi_i\phi_j\rangle \end{aligned} \quad (41)$$

8) *The major drawback of the Hartree approximation is that in this theory electrons are not identical and indistinguishable*, which violates one of the fundamental principles of quantum mechanics. As an example, consider a Hartree wavefunction of the helium atom in the first triplet excited state (3S):

$$|\Psi(1,2)\rangle = \phi_{1s}(1)\alpha(1)\phi_{2s}(2)\alpha(2) \quad (42)$$

If we interchange the coordinates of electrons 1 and 2, we obtain:

$$|\Psi(2,1)\rangle = \phi_{1s}(2)\alpha(2)\phi_{2s}(1)\alpha(1) \quad (43)$$

Clearly, the wavefunctions $|\Psi(1,2)\rangle$ and $|\Psi(2,1)\rangle$ are different, since the 1s and 2s orbitals have different radial distributions. As a result, the probability distributions $|\Psi(1,2)|^2$ and $|\Psi(2,1)|^2$ of finding electrons at positions \mathbf{r}_1 and \mathbf{r}_2 are also different, which proves that the electrons are not indistinguishable in the Hartree approximation.

9) What type of wavefunction allows electrons to be identical and indistinguish-

able? For the triplet state of the helium atom, there are two possibilities:

$$|\Psi(1,2)\rangle = \phi_{1s}\alpha(1)\phi_{2s}\alpha(2) + \phi_{1s}\alpha(2)\phi_{2s}\alpha(1) \quad (\text{symmetric}) \quad (44)$$

$$|\Psi(1,2)\rangle = \phi_{1s}\alpha(1)\phi_{2s}\alpha(2) - \phi_{1s}\alpha(2)\phi_{2s}\alpha(1) \quad (\text{antisymmetric}) \quad (45)$$

We find from spectroscopy that only one such triplet state exists in nature and it is the one corresponding to the antisymmetric wavefunction. More generally, *a many-electron wavefunction must be antisymmetric with respect to the interchange of the coordinates (both spatial and spin) of any two electrons.* This is also known as the generalization of the **Pauli exclusion principle**.