

Chapter 1

Adiabatic (Born-Oppenheimer) approximation

First write our the Hamiltonian for the nuclei-electron systems.

$$H = -\frac{1}{2} \sum_A \frac{\nabla_A^2}{M_A} + \frac{1}{2} \sum_{A \neq B} \frac{Z_A Z_B}{R_{AB}} - \sum_{i,A} \frac{Z_A}{r_{iA}} - \frac{1}{2} \sum_i \frac{\nabla_i^2}{m_e} + \sum_{i,j} \frac{1}{r_{ij}} \quad (1.0.1)$$

We aim at separating this problem into an electron problem *parametric* in the nuclei coordinates and a nuclei part.

First part of B-O approx: Write the total wavefunction as a product of a nuclear part $\nu(R)$ and an electronic part $\Psi(\{r\}; \{R\})$, where the semicolon represents the fact that the nuclear coordinates are *static parameters*.

$$\Phi(\{r\}, \{R\}) = \nu(\{R\}) \Psi(\{r\}; \{R\}) \quad (1.0.2)$$

Second part of B-O approx: determine $\Psi(\{r\}; \{R\})$ from the part of the Hamiltonian with *static nuclei* and *ignore cross terms of the nuclear kinetic operator with the electronic part of the wavefunction*.

$$H|\Phi(\{r\}, \{R\})\rangle = \left(\sum_A \frac{\nabla_A^2}{M_A} + \frac{1}{2} \sum_{A \neq B} \frac{Z_A Z_B}{R_{AB}} + H_{el}(r; R) \right) |\Psi(\{r\}; \{R\})\rangle |\nu(\{R\})\rangle \quad (1.0.3a)$$

$$\begin{aligned} &= \left[H_{el}(r; R) |\Psi(\{r\}; \{R\})\rangle + |\Psi(\{r\}; \{R\})\rangle \left(\sum_A -\frac{1}{2} \frac{\nabla_A^2}{M_A} + \frac{1}{2} \sum_{A \neq B} \frac{Z_A Z_B}{R_{AB}} \right) \right] |\nu(\{R\})\rangle \\ &\quad - \sum_A \frac{1}{2M_A} [|\nu(\{R\})\rangle \nabla_A^2 |\Psi(\{r\}; \{R\})\rangle + \nabla_A |\nu(\{R\})\rangle 2\nabla_A |\Psi(\{r\}; \{R\})\rangle] \end{aligned} \quad (1.0.3b)$$

$$= \left[H_{el}(r; R) |\Psi(\{r\}; \{R\})\rangle + |\Psi(\{r\}; \{R\})\rangle \left(\sum_A -\frac{1}{2} \frac{\nabla_A^2}{M_A} + \frac{1}{2} \sum_{A \neq B} \frac{Z_A Z_B}{R_{AB}} \right) \right] |\nu(\{R\})\rangle \quad (1.0.3c)$$

$$H_{el} = \sum_{i,A} \frac{Z_A}{r_{iA}} - \frac{1}{2} \sum_i \frac{\nabla_i^2}{m_e} + \sum_{i,j} \frac{1}{r_{ij}} \quad (1.0.3d)$$

In words: we want to solve the electronic problem for *static* nuclei. This will then create an effective potential for the nuclei. This effective potential is referred to as the adiabatic (Born-Oppenheimer) surface.

I am now going to drop labels of the set of nuclear coordinate $\{R\}$ to which a particular multi-electron wavefunction refers.

Chapter 2

Hartree Fock Method

2.1 Slater Determinants

Equation 1.0.3d is still a multi-body problem. In order to proceed, we must make an assumption on the nature of the electronic wavefunction $\Psi(\{r\})$. The simplest assumption is that the wavefunction is composed of a product of one electron wavefunctions:

$$\Psi(\{r\}) = |\chi_1(r_1)\chi_2(r_2)\chi_3(r_3)\cdots\rangle \quad (2.1.1)$$

This is known as a Hartree product.

The problem with equation 2.1.1 is that it gives electrons an identity. In other words, if I swap two electrons I get a wavefunction with potentially different properties. In still other words, the wavefunction is not a fermionic wavefunction as it is not antisymmetric under exchange of electrons. Therefore the simplest *physical* wavefunction has form:

$$\Psi(\{r\}) = \sqrt{\frac{1}{N!}} \sum_n^{n=N!} ((-1)^{p_n} \mathcal{P}_n(\chi_1(r_1)\chi_2(r_2)\cdots)) \quad (2.1.2)$$

where \mathcal{P}_n represents the permutations operator for electron coordinates and p_n represents the parity (even-ness) of the number of permutations. A more convenient way of representing the same equation is:

$$\Psi(\{r\}) = \sqrt{\frac{1}{N!}} \begin{vmatrix} \chi_1(r_1) & \chi_2(r_1) & \cdots & \chi_n(r_1) \\ \chi_1(r_2) & \chi_2(r_2) & \cdots & \chi_n(r_2) \\ \vdots & & \ddots & \\ \chi_n(r_n) & & \cdots & \chi_n(r_n) \end{vmatrix} \quad (2.1.3)$$

To cut down on the suffix-madness such a Slater determinant will be referred to as:

$$|\chi_1\chi_2\chi_3\cdots\chi_n\rangle \quad (2.1.4)$$

The Hartree Fock method consists in finding the variational value of the electronic energy for such a wavefunction.

2.2 Manipulating Slater Determinants

Most of the efforts in quantum chemistry are concerned with finding expectation values between Slater determinants and the Hamiltonian from equation 1.0.3d. There are two parts in that Hamiltonian, one which depends on one electron only $\mathcal{O}_1 = \sum_i h(r_i) = \sum_{i,A} \frac{Z_A}{r_{iA}} - \frac{1}{2} \sum_i \frac{\nabla_i^2}{m_e}$ and one which depends on pairs of electrons: $\mathcal{O}_2 = \sum_{i,j} \frac{1}{r_{ij}}$.

Let us consider what the expectation value of \mathcal{O}_1 is.

$$\langle \Psi(\{r\}) | \mathcal{O}_1 | \Psi(\{r\}) \rangle = \langle \Psi(\{r\}) | \sum_i h(r_i) | \Psi(\{r\}) \rangle \quad (2.2.1a)$$

$$= N \langle \Psi(\{r\}) | h(r1) | \Psi(\{r\}) \rangle \quad (2.2.1b)$$

This manipulation is possible because all electron coordinates are indistinguishable from each other (thank you anti-symmetry!). Each Slater determinant is composed of $N!$ permutations of spin orbitals $\chi_n(r_j)$. When we are integrating over the variables $r2, r3, r4$ etc. those variable must appear in the same order in both wavefunctions. This is because of the orthonormality of the one electron spin orbitals. In other words:

$$\int dr^2 \chi_i^*(r2) \chi_j^*(r2) = \delta_{ij} \quad (2.2.2)$$

For a particular spin orbital $\chi(r1)$ associated with $r1$ there will be $(N - 1)!$ such combinations. All $(N - 1)!$ combinations integrate to 1. Hence:

$$\langle \Psi(\{r\}) | \mathcal{O}_1 | \Psi(\{r\}) \rangle = \sum_i N(N - 1)!(N!)^{-1} \langle \chi_i(r1) | h(r1) | \chi_i(r1) \rangle \quad (2.2.3)$$

In a paroxysm of laziness, this equation is further simplified by another piece of notation: we drop the electron coordinates altogether, and drop the χ :

$$\langle \Psi(\{r\}) | \mathcal{O}_1 | \Psi(\{r\}) \rangle = \sum_i \langle i | h | i \rangle \quad (2.2.4)$$

What about \mathcal{O}_2 ? In this case the operators involve always *pairs* of electrons:

$$\mathcal{O}_2 = r_{12} + r_{13} + r_{14} + \dots \quad (2.2.5)$$

Again, each coordinate is undistiguishable, so we can write:

$$\mathcal{O}_2 = \frac{N(N - 1)}{2} r_{12} \quad (2.2.6)$$

So:

$$= \frac{N(N - 1)}{2} (N!)^{-1} \int \sum_m \sum_{n \neq m} (-1)^{p_m + p_n} \mathcal{P}_m(\chi_1^*(r1) \chi_2^*(r2) \dots) \frac{1}{r_{12}} \mathcal{P}_n(\chi_1(r1) \chi_2(r2) \dots) \quad (2.2.7)$$

Given that the spin orbitals χ_m and χ_n are associated with coordinates $r1$ and $r2$, orthonormality of the spin orbitals means there are only $(N - 2)!$ permutations of the other integration variables that integrate to 1. Therefore:

$$= \frac{1}{2} \sum_m \sum_{n \neq m} \int dr1 dr2 \chi_m^*(r1) \chi_n^*(r2) \frac{1}{r_{12}} (\chi_m(r1) \chi_n(r2) - \chi_n(r1) \chi_m(r2)) \quad (2.2.8)$$

Again, this expression is a pain to write out, so we use some notation two re-express it:

$$\langle ij | kl \rangle = \int dr1 dr2 \chi_i^*(r1) \chi_j^*(r2) \frac{1}{2} \chi_k(r1) \chi_l(r2) \quad (2.2.9)$$

Also:

$$\langle ij || kl \rangle = \langle ij | kl \rangle - \langle ij | lk \rangle \quad (2.2.10)$$

So with this beautiful notation we can concisely write the expectation value of a single Slater determinant with the Hamiltonian:

$$\langle \Psi(\{r\}) | H | \Psi(\{r\}) \rangle = \sum_i \langle i | h | i \rangle + \frac{1}{2} \sum_m \sum_{n \neq m} \langle mn || mn \rangle \quad (2.2.11)$$

Minor point: since $\langle mm || mm \rangle = 0$, we could drop the $n \neq m$ condition.

NB: All the integrations over r still contains integration over the spin coordinates!!!

2.3 Integrating out spin

Let us think up an example: the energy of a Lithium atom in the ground state. Let us imagine two electrons occupy a spatial orbital $|1\rangle$ and the third is in some different orbital $|2\rangle$, I shall express spin by a bar. So therefore our wavefunction is:

$$\Psi(\{r\}) = |1\bar{1}2\rangle \quad (2.3.1)$$

Spin does not matter one hoot when calculating the one electron part: spin simply integrates out! Therefore:

$$\langle \Psi(\{r\}) | \mathcal{O}_1 | \Psi(\{r\}) \rangle = 2 \langle 1|h|1\rangle + \langle 2|h|2\rangle \quad (2.3.2)$$

what about the two electron part?

$$\begin{aligned} \langle \Psi(\{r\}) | \mathcal{O}_2 | \Psi(\{r\}) \rangle &= \frac{1}{2} (\\ &\langle 1\bar{1}|1\bar{1}\rangle - \langle 1\bar{1}|\bar{1}1\rangle + \langle 12|12\rangle - \langle 12|21\rangle + \\ &\langle \bar{1}1|\bar{1}1\rangle - \langle \bar{1}1|1\bar{1}\rangle + \langle \bar{1}2|\bar{1}2\rangle - \langle \bar{1}2|2\bar{1}\rangle \\ &\langle 21|21\rangle - \langle 21|12\rangle + \langle 2\bar{1}|2\bar{1}\rangle - \langle 2\bar{1}|\bar{1}2\rangle) = \\ &0.5(\langle 1\bar{1}|1\bar{1}\rangle + \langle 12|12\rangle - \langle 12|21\rangle + \\ &\langle \bar{1}1|\bar{1}1\rangle + \langle \bar{1}2|\bar{1}2\rangle \\ &\langle 21|21\rangle - \langle 21|12\rangle + \langle 2\bar{1}|2\bar{1}\rangle) \end{aligned} \quad (2.3.3)$$

(2.3.4)

Let us introduce another two pieces of shorthand: coulomb and exchange integrals. The Coulomb integral:

$$J_{ab} = \langle ab|ab\rangle \quad (2.3.5)$$

The exchange integral:

$$K_{ab} = \langle ab|ba\rangle \quad (2.3.6)$$

Using these definitions we can write the energy of the Lithium atom as:

$$= 2 \langle 1|h|1\rangle + \langle 2|h|2\rangle + 2J_{11} - K_{11} + 2J_{12} - K_{12} \quad (2.3.7)$$

this is because $K_{11} = J_{11}$.

So in other words, the Coulomb operator operates over *all* pairs of electrons, irrespective of spin whereas the Exchange operator operates only for pairs of equal spin. It also seems that exchange avoids self interaction of electrons by the Coulomb operator.

2.4 Variational solution of the Hartree Fock problem

We want to minimise the expression:

$$E_0[\{\chi\}] = \sum_i \langle i|h|i\rangle + \frac{1}{2} \sum_m \sum_n \langle mn||mn\rangle \quad (2.4.1)$$

with respect to the one electron spin orbitals $\chi_1\chi_2\dots$ given the condition:

$$\int dr_1 \chi_a^*(r_1) \chi_b(r_1) = [a|b] = \delta_{ab} \quad (2.4.2)$$

Let us construct the variational functional:

$$\mathcal{L}[\{\chi\}] = E_0[\{\chi\}] - \sum_a \sum_b \epsilon_{ab} ([a|b] - \delta_{ab}) \quad (2.4.3)$$

Let us make a small variation of the orbitals $\{\delta\chi\}$. The corresponding variation in the functional \mathcal{L} must be zero hence:

$$\delta E_0[\{\chi\}] = \sum_a \sum_b \epsilon_{ab} \delta[a|b] \quad (2.4.4)$$

Let us evaluate the left hand side of this equation:

$$\delta E_0[\{\chi\}] = \sum_a \langle (\delta a)|h|a \rangle + \sum_a \sum_b \langle (\delta a)b|ab \rangle - \langle (\delta a)b|ba \rangle + c.c. \quad (2.4.5)$$

NOTE: the factor of half has disappeared!

We want to extricate the (δa) terms from this equation. In order to do so, let us define two one electron operators: the Coulomb and Exchange operators:

$$\mathcal{J}_a(r1)|b \rangle = \int dr1 \chi_a(r1) \chi_a^*(r1) \chi_b(r2) \quad (2.4.6)$$

The exchange operator is wierder:

$$\mathcal{K}_a(r1)|b \rangle = \int dr1 \chi_a(r1) \chi_b^*(r1) \chi_a(r2) \quad (2.4.7)$$

Both operators depend on the electron wavefunction, making them wierd “1 electron” operators. The exchange operator actually depends on the spin orbitals it operates on and is therefore non-local! The Coulomb operator \mathcal{J}_a is clearly expressing the mean coulomb attraction from an electron in spin-orbital χ_a . Exchange cannot be so clearly understood: it is present only because of the anti-symmetric nature of the wavefunction. It cancels out the Coulomb attraction of a spin orbital with itself (though to me this seems like a piece of sleight of hand, depending on dropping the $m \neq n$. More importantly, it reduces the repulsion between electrons of parallel spin. Using these convenient devices the equation for \mathcal{L} is written:

$$\delta \mathcal{L} = \sum_a \int dr1 \delta \chi_a^*(r1) \left(h(r1) \chi_a(r1) + \sum_b (\mathcal{J}_b(r1) - \mathcal{K}_b(r1)) \chi_a(r1) - \sum_b \epsilon_{ab} \chi_b(r1) \right) + c.c. \quad (2.4.8)$$

Here comes a slightly subtle bit: since the variations are arbitrary, and are independent of each others complex conjugate, the integrand itself must evaluate to zero.

$$\left(h(r1) + \sum_b (\mathcal{J}_b(r1) - \mathcal{K}_b(r1)) \right) \chi_a(r1) = \sum_b \epsilon_{ab} \chi_b(r1) \quad (2.4.9)$$

We’re almost there! The operator: $h(r1) + \sum_b (\mathcal{J}_b(r1) - \mathcal{K}_b(r1))$ is simply the fock operator $f(r1)$. In order to put this equation in Canonical form, we must have the Lagrange multipliers ϵ_{ab} as a diagonal matrix.

2.5 Canonical Hartree Fock equations

Consider an arbitrary unitary transformation U of the spin orbitals. The Fock operator is unvariant under such a transformation. The one electron part h is clearly independent of it, let us consider the exchange operator (for the coulomb operator this is shown in page 122).

$$\chi'_b(r1) = \sum_c U_{cb} \chi_c(r1) \quad (2.5.1a)$$

$$\sum_a \mathcal{K}_a(r1) \chi_b(2) = \int dr1 \sum_a \chi_a^*(r1) \chi_b(r1) \chi_a(2) \quad (2.5.1b)$$

$$\sum_a \mathcal{K}'_a(r1) \chi'_b(2) = \int dr1 \sum_a \left(\sum_i U_{ai}^* \chi_i^*(r1) \right) \left(\sum_j U_{jb} \chi_j(r1) \right) \chi'_a(2) \quad (2.5.1c)$$

$$= \int dr1 \sum_{ij} \sum_a U_{ai}^* U_{jb} \chi_i^*(r1) \chi_j(r1) \chi'_a(2) = \int dr1 \sum_i \chi_i^*(r1) \chi_i(r1) \chi'_a(2) \quad (2.5.1d)$$

From the fundamental property of a unitary matrix.

So if we take equation 2.4.9 and left multiply it by χ_c , we get:

$$\langle \chi_c | f(r1) | \chi_a \rangle = \epsilon_{ca} \quad (2.5.2)$$

Since this ϵ_{ca} is a Hermitian matrix (consequence of the definition of the variational functional), it is always possible to define a unitary transformation that diagonalises and leaves the fock operator (and hence our variational energy) intact. So typically the canonical problem we solve is:

$$f(r1) | \chi_a \rangle = \epsilon_{aa} | \chi_a \rangle \quad (2.5.3)$$

This is a rather important point in HF: the spin orbitals which we usually call molecular orbitals, are not the only orbitals who can construct a Slater determinant with variational energy. They just happen to be the ones that diagonalise the fock matrix (defined as $F_{ab} = \langle \chi_a | f(r1) | \chi_b \rangle$). We can take any rotation of those orbitals and still have the same total energy: nothing is special about molecular orbitals and they mean *almost* nothing.

2.6 Self Consistent method and LCAO

Equation 2.5.3 says that if we construct a Slater determinant with spin orbitals which diagonalise the Fock operator, the energy of that Slater determinant is the lower than or equal to any energy described by a Slater determinant. The catch 22 is that the fock operator itself depends on the spin orbitals! We also need to find a representation for the 1 electron operator f , which as we can see will be achieved by using a basis set.

In order to get to a practical computational method to solve this problem it is also important to write down the spin orbitals in term of some basis set. Without getting into the detail of *why* pick a certain basis set rather than another, let us assume that the spatial part of the spin orbitals has been written as a linear position of some basis set $\{\phi\}$.

$$| \chi_a \rangle = \sum C_{ia} \phi_i \quad (2.6.1)$$

Also we shall need to know the overlap matrix of this basis set:

$$\langle \phi_j | \phi_i \rangle = S_{ij} \quad (2.6.2)$$

So let us write integrate the spin degrees of freedom out of the Fock operator (just ass for the case if Lithium solved earlier) for a closed shell system (one with all electrons paired in the same spatial orbitals):

$$f(r1) = h(r1) + \sum_a^{a=N/2} (2\mathcal{J}_a(r1) - \mathcal{K}_b(r1)) \quad (2.6.3)$$

This can easily be derived bearing in mind that exchange interactions exist only between pairs with similar spin.

Let us rewrite equation 2.5.3 for a general non-orthogonal basis:

$$f(r1) | \chi_a \rangle = f(r1) \sum C_{ia} \phi_i = \epsilon_a \sum C_{ia} \phi_i \quad (2.6.4)$$

now left multiply this equation by ϕ_j^* and integrate:

$$\int dr1 \phi_j^*(r1) f(r1) \sum C_{ia} \phi_i(r1) = \epsilon_a \sum C_{ia} \int \phi_j^*(r1) \phi_i(r1) \quad (2.6.5)$$

writing it in matrix form:

$$\sum F_{ji} C_{ia} = \epsilon_a \sum S_{ji} C_{ia} \quad (2.6.6)$$

[I should rewrite the previous part using greek letters for the basi set but cannot be bothered].

Let us evaluate 2.6.3 for a particular basis set:

$$F_{\mu\nu} = \langle \phi_\mu | h | \phi_\nu \rangle + \sum_a^{a=N/2} (2 \langle \mu a | \nu a \rangle - \langle \mu a | a \nu \rangle) \quad (2.6.7)$$

remember all the spatial orbitals:

$$\chi_a = C_{\lambda a} \phi_\lambda \quad (2.6.8)$$

so:

$$F_{\mu\nu} = \langle \phi_\mu | h | \phi_\nu \rangle + \sum_a \sum_{\lambda\sigma}^{a=N/2} (C_{a\lambda} C_{a\sigma}^*) (2 \langle \mu\sigma | \nu\lambda \rangle - \langle \mu\sigma | \lambda\nu \rangle) \quad (2.6.9)$$

$$F_{\mu\nu} = \langle \phi_\mu | h | \phi_\nu \rangle + \sum_{\lambda\sigma} P_{\lambda\sigma} (\langle \mu\sigma | \nu\lambda \rangle - 0.5 \langle \mu\sigma | \lambda\nu \rangle) \quad (2.6.10)$$

This is it! We have written our Fock operator in a particular matrix representation, using a particular non-orthogonal basis set. The Fock matrix has a one electron part $\langle \phi_\mu | h | \phi_\nu \rangle$ which can be calculated once at the beginning of the computation. We first make a guess for the orbitals, then construct the two electron density matrix $P_{\lambda\sigma}$, from this and the hideous 2 electron integrals $\langle \mu\sigma | \lambda\nu \rangle$ we construct F , solve the generalised eigenvalue problem $FC = SCe$, plug the solution back into the density matrix and keep going until subsequent density matrices are consistent.

2.7 Koopmans Theorem

It has been said that the orbitals which diagonalise the Fock matrix are meaningless. In fact they have one clear meaning: they are connected to the ionization energy of a molecule. Consider a system with $2N$ electrons in N closed shells, then:

$$E0 = \sum_a 2 \langle a|h|a \rangle + \sum_a \sum_b 2 \langle ab|ab \rangle - \langle ab|ba \rangle \quad (2.7.1)$$

What if we remove an electron from the the N th orbital, leaving all other orbitals untouched (frozen orbital approximation)? What will the energy of such a determinant be?

$$E+ = \sum_{a \neq N} 2 \langle a|h|a \rangle + \langle N|h|N \rangle + \left(\sum_{a \neq N} \sum_{b \neq N} 2 \langle ab|ab \rangle - \langle ab|ba \rangle \right) + \sum_{b \neq N} 2 \langle Nb|Nb \rangle - \langle Nb|bN \rangle \quad (2.7.2)$$

So:

$$E + -E0 = \langle N|h|N \rangle + \left(\sum_c 2 \langle Nc|Nc \rangle - \langle Nc|cN \rangle \right) = \epsilon_N \quad (2.7.3)$$

2.8 Closing Remarks

I have been very sloppy with nomenclature. This is basically a rather bad paraphrase of Szabo and Ostlund. USE AT OWN PERIL.

Bibliography

- [1] A. Szabo and N. Ostund, *Modern Quantum Chemistry*, Dover Publications 1982