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Contents

1 Many-body atomic physics

1.1 Independent particle model, slater determinants

Main ref: Lindgren & Morrison chap 5.

The N -electrons atomic Hamiltonian, with nuclear charge Z , can be written (in atomic units)

$$H = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 - \sum_{i=1}^N \frac{Z}{r_i} + \sum_{i<j}^N \frac{1}{r_{ij}} + V_{\text{mag}}. \quad (1.1)$$

Even if we have no magnetic potential ($V_{\text{mag}}=0$, ie no magnetic interactions) this Hamiltonian is complicated for more than say two electrons. We introduce a further approximation and say that the electrons moves independently of the other electrons in an *average* field caused by the atomic nucleus and the electrons. This approximation is what we call the *independent-particle model*. We express this mathematically by writing the Hamiltonian as a sum of two parts

$$H = H_0 + V_{\text{es}}, \quad (1.2)$$

and we ignore magnetic interactions for the moment. The first term

$$H_0 = \sum_{i=1}^N h_0(i) \quad (1.3)$$

is a sum of one-electron operators

$$h_0(i) = -\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i} + u(\mathbf{r}_i), \quad (1.4)$$

and the last term is

$$V_{\text{es}} = - \sum_i u_i(\mathbf{r}_i) + \sum_{i>j}^N \frac{1}{r_{ij}}. \text{ SHOULD IT BE } i < j \text{ ???} \quad (1.5)$$

The first term H_0 is an approximate Hamiltonian which is supposed to describe the average interaction, and V_{es} is a departure from this approximate single-particle description and will be treated as a perturbation. This means that V_{es} has to be reasonably small (for perturbation theory to apply), and for this to be the case the average potential $u(\mathbf{r}_i)$ should contain most of the Coulomb repulsion between the electrons.

We describe the system of N electrons in the average potential by a product wave function

$$\Psi = \phi_a(1)\phi_b(2)\dots\phi_n(N), \quad (1.6)$$

and according to LM this is also the “simplest” such wave function. The letters a, b, \dots shall represent the set of quantum numbers necessary to specify a single-electron state, and the numbers $1, 2, \dots$ stand for the space and spin coordinates for electrons numbered $1, 2, \dots$, so that $\phi_a(1) = \psi_a(x_1)\chi_1(1)$ represents electron 1 in state a , at position x_1 and with spin χ_1 (“up” or “down”). So if a single electron wavefunction satisfy

$$h_0(1)\phi_a(1) = \left[-\frac{1}{2}\nabla_1^2 - \frac{Z}{r_1} + u(\mathbf{r}_1) \right] \phi_a(1) = \varepsilon_a \phi_a(1), \quad (1.7)$$

then the product wavefunction Ψ is an eigenfunction of the approximate Hamiltonian

$$H_0\Psi = \sum_{i=1}^N \left[-\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i} + u(\mathbf{r}_i) \right] \Psi = E_0\Psi, \quad (1.8)$$

where $E_0 = \sum_{i=1}^N \varepsilon_i$.

1.1.1 Slater determinants and antisymmetrisation

But every product state $\tilde{\Psi}$ consisting of permutations of the single electron states in Ψ (Eq. (??)) is also an eigenstate to H_0 with the same eigenvalue E_0 ! From the Pauli exclusion principle a many-electron system must be *antisymmetric* with respect to interchange of any two electrons (or fermions in general). To form such an antisymmetric wave function we introduce the *Slater determinant*

$$\Phi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_a(1)\phi_a(2)\dots\phi_a(N) \\ \phi_b(1)\phi_b(2)\dots\phi_b(N) \\ \vdots \\ \phi_n(1)\phi_n(2)\dots\phi_n(N) \end{vmatrix}. \quad (1.9)$$

Evaluating the determinant we get a sum of product states and each term in the sum is an eigenfunction of H_0 , with eigenvalue E_0 , so Φ must also have this property. Any interchange of two electrons amounts to an interchange of two

columns in the Slater determinant, and this leads to an appropriate antisymmetric sign change by the properties of determinants. The Slater determinant also enforces the exclusion principle, since if any two single-electron states are the same, there will be two identical rows in the determinant and it will vanish (by determinant properties again). The prefactor $1/\sqrt{N!}$ ensures normalisation (we have $N!$ permutations).

To construct a Slater determinant we need to know which single-particle states are occupied, and decide on how to order them in the determinant. In Dirac notation we write

$$|\Phi\rangle = |\{abc \dots n\}\rangle, \quad (1.10)$$

letting the curly brackets stand for the Slater determinant antisymmetrisation, so that

$$|\{abc \dots n\}\rangle = -|\{bac \dots n\}\rangle \quad (1.11)$$

and so on.

1.2 Matrix elements between Slater determinants

We are interested in the atomic Hamiltonian, and it contains one particle operators of the type Z/r_i and two particle operators of the kind $1/r_{ij}$. In particular we will work with sums of such operators, and we will call sums of general one particle operators $f(i)$ for $F = \sum_i f(i)$ and sums of general two particle operators $g(i, j)$ for $G = \sum_{i < j} g(i, j)$. Note how the sum includes each *pair* of electrons only once. To work out some examples we will restrict ourselves to the two particle case (two electrons), so that

$$\begin{aligned} F &= f(1) + f(2), \\ G &= g(1, 2). \end{aligned} \quad (1.12)$$

The examples will be fully worked out on paper. If we do this we will find that the diagonal matrix element for F between $|\{ab\}\rangle$ is

$$\langle\{ab\}|F|\{ab\}\rangle = \langle a|f|a\rangle + \langle b|f|b\rangle, \quad (1.13)$$

which is what we would have gotten if we had looked at ordinary product functions $\phi_a(1)\phi_b(2)$ rather than the antisymmetric determinant state $|\{ab\}\rangle$.

A nondiagonal element between determinantal states differing by a single state is shown to be

$$\langle\{ab\}|F|\{ac\}\rangle = \langle b|f|c\rangle, \quad (1.14)$$

and with states differing by two we get

$$\langle\{ab\}|F|\{cd\}\rangle = 0. \quad (1.15)$$

The diagonal matrix element for the two particle operator $G = g(1, 2)$ is shown to be

$$\langle \{ab\} | G | \{ab\} \rangle = \langle ab | g | ab \rangle - \langle ba | g | ab \rangle. \quad (1.16)$$

The first matrix element of g in the above equation (??) is called the *direct* term and the second is called the *exchange* term. This last exchange term would *not* occur if we used a non-determinantal product state $\phi_a(1)\phi_b(2)$.

1.3 Some new notation to generalise

We can generalise the previous results for a two-electron system to N -electrons, and to aid in doing this we introduce new notation. We let Greek letters label ordered sets of quantum numbers representing Slater determinants. If α represents a, b, c, \dots, n we write the determinantal state as¹

$$|\alpha\rangle = |\{abc, \dots, n\}\rangle. \quad (1.17)$$

We proceed and say that $|\alpha_a^r\rangle$ denotes a determinant state in which an occupied orbital a in α is replaced by an excited orbital r . We also have double substitution (excitation?) written as $|\alpha_{ab}^{rs}\rangle$ and so on.

Using this new notation we can generalise the results for the two-particle matrix elements from the previous section. For diagonal matrix elements of single and two-particle operators F, G we get

$$\langle \alpha | F | \alpha \rangle = \sum_a^{\text{occ}} \langle a | f | a \rangle, \quad (1.18)$$

ie with a sum ranging over all occupied orbitals, and

$$\langle \alpha | G | \alpha \rangle = \sum_{a < b}^{\text{occ}} [\langle ab | g | ab \rangle - \langle ba | g | ab \rangle], \quad (1.19)$$

where the sum ranges over all pairs of occupied orbitals a, b only *once*. We could also write this as

$$\langle \alpha | G | \alpha \rangle = \frac{1}{2} \sum_a^{\text{occ}} \sum_b^{\text{occ}} [\langle ab | g | ab \rangle - \langle ba | g | ab \rangle], \quad (1.20)$$

¹LM then claims that we should call *single-particle functions*, that appear in the determinant, for *occupied* orbitals, and the “remaining set” for *excited/virtual* orbitals. But what does this mean? Isn’t every factor function $\phi_x(i), x \in abc \dots n$ only a single particle function? The answer to this is that it is poor language in LM. The “remaining set” refers not to the set abc, \dots, n , but to all possible states in the atom (or continuum I guess). Every orbital that is put in a Slater determinant is supposed to be a single electron function.

with a factor of half compensating for counting each pair twice.

For non-diagonal elements between states differing by a single orbital we get

$$\begin{aligned}\langle \alpha_a^r | F | \alpha \rangle &= \langle r | f | a \rangle, \\ \langle \alpha_a^r | G | \alpha \rangle &= \sum_b^{\text{occ}} [\langle r b | g | a b \rangle - \langle b r | g | a b \rangle].\end{aligned}\quad (1.21)$$

Note how this (naturally) removes the sum over a compared to the diagonal case. For states differing by two elements we get

$$\begin{aligned}\langle \alpha_{ab}^{rs} | F | \alpha \rangle &= 0, \\ \langle \alpha_{ab}^{rs} | G | \alpha \rangle &= \langle rs | g | ab \rangle - \langle sr | g | ab \rangle.\end{aligned}\quad (1.22)$$

Since G is a two-particle operator and F is a one-particle operator, matrix elements between states differing by more than two vanishes.

1.4 The Hartree-Fock equations

The variational principle tells us that we can find the “best” approximation to the ground state of some system, with Hamiltonian H , by minimising the expectation value of the energy,

$$\langle E \rangle = \langle 0 | H | 0 \rangle. \quad (1.23)$$

If we look to find the ground state Slater determinant $|\alpha\rangle$ of an atomic system we look at the energy expectation value (ignoring magnetic effects)

$$\langle E \rangle = \langle \alpha | \sum_{i=1}^N \left(-\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i} \right) + \sum_{i<j}^N \frac{1}{r_{ij}} | \alpha \rangle, \quad (1.24)$$

with the condition that this expectation value is *stationary* with respect to small changes in the orbitals of $|\alpha\rangle = |\{abcd \dots n\}\rangle$. We will use this condition to derive the Hartree-Fock (HF) equations.

The small change in the orbital $|a\rangle$ can be expressed by

$$|a\rangle \rightarrow |a\rangle + \eta |r\rangle, \quad (1.25)$$

where η is a small real number. Earlier we said that a Slater determinant in which orbital a is replaced by excitation r is labeled $|\alpha_a^r\rangle$, and so this small change in the orbital can be written a small change in the Slater determinant,

$$|\alpha\rangle \rightarrow |\alpha\rangle + \eta |\alpha_a^r\rangle. \quad (1.26)$$

Thus the corresponding energy expectation value after the small change is

$$(\langle \alpha | + \eta \langle \alpha_a^r |) H (| \alpha \rangle + \eta | \alpha_a^r \rangle) = \langle E \rangle + \eta (\langle \alpha_a^r | H | \alpha \rangle + \langle \alpha | H | \alpha_a^r \rangle), \quad (1.27)$$

where we the terms quadratic in η , since η is taken to be small “enough”. We now note that H is Hermitian so that the two “change”-terms are equal, thus the RHS in equation (??) becomes

$$\langle E \rangle + \eta (\langle \alpha_a^r | H | \alpha \rangle + \langle \alpha | H | \alpha_a^r \rangle) = \langle E \rangle + 2\eta \langle \alpha_a^r | H | \alpha \rangle. \quad (1.28)$$

So the condition that the energy expectation value is stationary (ie doesn’t change) due to a small change in orbitals, amounts to saying that

$$\langle \alpha_a^r | H | \alpha \rangle = 0. \quad (1.29)$$

This is called *Brillouin’s theorem* (1933,1934), and means that there are no matrix elements of H between $| \alpha \rangle$ and states with *single substitution*. We will see that it implies that there is no first-order mixing of such states (whatever that might mean).

We can write this condition in a more direct way, using the expressions for single- and two-particle matrix elements of N -electron systems from the previous section. Writing out the atomic Hamiltonian explicitly the condition becomes

$$\langle \alpha_a^r | \sum_{i=1}^N \left(-\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i} \right) | \alpha \rangle + \langle \alpha_a^r | \sum_{i<j}^N \frac{1}{r_{ij}} | \alpha \rangle = 0, \quad (1.30)$$

where the first term is made up of sums of one-particle operators, and the second term is a sum of two-particle operators. Using the expressions for matrix elements of such operators in Equation (??) we get that the condition can be written

$$\langle r | -\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i} | a \rangle + \left[\sum_b^{\text{occ}} \left(\langle r b | \frac{1}{r_{ij}} | a b \rangle - \langle b r | \frac{1}{r_{ij}} | a b \rangle \right) \right] = 0. \quad (1.31)$$

We should note that the label r for the excited orbital is not related to r_i or r_{ij} . LM drops the index on r_i and sets r_{ij} to r_{12} from this point onwards, but it’s not clear to me yet why this can be done? Maybe we are putting the i -dependence into $h_{\text{HF}}, u_{\text{HF}}$ (see below)? No, it rather is that electron i is the electron of orbital $| a \rangle$, and summing over occupied states b we are summing over electrons j ?

We further want to simplify things by introducing a Hartree-Fock operator (h_{HF}) and Hartree-Fock potential (u_{HF}) by defining

$$h_{\text{HF}} = -\frac{1}{2} \nabla^2 - \frac{Z}{r} + u_{\text{HF}}, \quad (1.32)$$

$$\langle i | u_{\text{HF}} | j \rangle = \sum_b^{\text{occ}} \left(\langle i b | \frac{1}{r_{12}} | j b \rangle - \langle b i | \frac{1}{r_{12}} | j b \rangle \right).$$

Then we can write the Brillouin condition as

$$\langle r | h_{\text{HF}} | a \rangle = 0. \quad (1.33)$$

We can show (I want to do this later) that h_{HF} is Hermitian and unitary, and thus we can find a basis (orbitals) $\{|a'\rangle\}$ such that h_{HF} is diagonal, and

$$h_{\text{HF}} |a'\rangle = \varepsilon'_a |a'\rangle. \quad (1.34)$$

This eigenvalue equation is called in LM “the normal form of the Hartree-Fock equation”. Dropping the primes for convenience (we remember that we are dealing with the basis in which h_{HF} is diagonal) we can write explicitly

$$\left(-\frac{1}{2} \nabla^2 - \frac{Z}{r} + u_{\text{HF}} \right) |a\rangle = \varepsilon_a |a\rangle. \quad (1.35)$$

This equation is nice since each term can be given a simple physical interpretation. The first term is the kinetic energy of the electron, and the second term represents the attraction due to the atomic nucleus. The third term, the potential u_{HF} , represents the average effect of the Coulomb interaction of the electron represented by $|a\rangle$ with the rest of the atomic electrons, *including the exchange interaction*.

Next up is to identify the physical meaning of the eigenvalue ε_a in the normal form Hartree-Fock Equation (??).

1.5 Koopmans' Theorem

The total energy of an atomic state represented by a Slater determinant $|\alpha\rangle$ is represented by the expectation value

$$\langle E_{\text{atom}} \rangle = \langle \alpha | H | \alpha \rangle. \quad (1.36)$$

We know the explicit form of the Hamiltonian, a sum of one- and two-particle operators, so we can play the same game as we did when simplifying $\langle \alpha_a^r | H | \alpha \rangle$, but with diagonal elements. From equations (??) and (??) we get that

$$\langle E_{\text{atom}} \rangle = \langle \alpha | \sum_{i=1}^N \left(-\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i} \right) + \sum_{i<j}^N \frac{1}{r_{ij}} | \alpha \rangle \quad (1.37)$$

becomes

$$\begin{aligned} \langle E_{\text{atom}} \rangle &= \sum_b^{\text{occ}} \langle b | \left(-\frac{1}{2} \nabla^2 - \frac{Z}{r} \right) | b \rangle \\ &+ \frac{1}{2} \sum_{bc}^{\text{occ}} (\langle bc | r_{12}^{-1} | bc \rangle - \langle cb | r_{12}^{-1} | bc \rangle). \end{aligned} \quad (1.38)$$

Consider now the same energy expectation value $\langle E_{\text{ion}} \rangle$ for the same atom but with orbital $|a\rangle$ removed; an atomic ion. We assume that this removal doesn't affect the other orbitals in any way. The difference between the expectation values then is exactly the terms regarding orbital $|a\rangle$ in Equation (??),

$$\langle E_{\text{atom}} \rangle - \langle E_{\text{ion}} \rangle = \langle a | \left(-\frac{1}{2} \nabla^2 - \frac{Z}{r} \right) | a \rangle + \sum_b^{\text{occ}} (\langle ab | r_{12}^{-1} | ab \rangle - \langle ba | r_{12}^{-1} | ab \rangle). \quad (1.39)$$

The factor $\frac{1}{2}$ disappears from the second term since we have a contribution from a in both the sum over b and over c in Equation (??), and $\langle ab | g | ab \rangle = \langle ba | g | ba \rangle$ and $\langle ba | g | ab \rangle = \langle ab | g | ba \rangle$. Is this correct?

But now we need to recall how we defined the HF operator h_{HF} , Equation (??)! We now see that the RHS of Equation (??) is in fact $\langle a | h_{\text{HF}} | a \rangle$. And $h_{\text{HF}} | a \rangle = \varepsilon_a | a \rangle$ (recall that we can express orbital a in a basis such that h_{HF} is diagonal). So the difference in energy between atom and ion is

$$\langle E_{\text{atom}} \rangle - \langle E_{\text{ion}} \rangle = \langle a | h_{\text{HF}} | a \rangle = \langle a | \varepsilon_a | a \rangle = \varepsilon_a \langle a | a \rangle = \varepsilon_a. \quad (1.40)$$

What we have found here is that the eigenvalue of the Hartree-Fock (HF) operator is the negative work required to remove one electron from the atomic system. Another way to phrase this is to say that the eigenvalue of h_{HF} is the negative of the *binding energy*. This result is called Koopman's Theorem (Koopmans 1933).

The important assumption we used here with the removal of one electron not affecting the other orbitals is not physically accurate. The system should "readjust" or "relax" to the removal of an electron. The theorem is only valid if we can neglect the effect of this "relaxation".