3   Multi-electron atoms and Hartree-Fock model

Important to note: this is **not** a general overview to atomic physics. There are many extremely important topics I am not discussing at all, e.g., spin-orbit effect, theory of angular momentum addition and coupling etc., which are crucial for understanding quantum mechanics of atoms. However, those are essentially regular quantum mechanics, which you have seen in other courses, and do not require a computer. Here, I focus on the aspects of many-body atomic physics for which computational calculations are essential. Some excellent sources to pursue these other topics in more detail are books by Sakurai[1], Johnson[2], Sobelman[3], and Bethe and Salpeter[4], which are available in the library.

3.1   Many-particle quantum mechanics

3.1.1   Exchange symmetry, product states

This is only a quick review; see Chapter 7 of Sakurai[5] for a more complete discussion (or any other QM textbook).

Consider system of two non-interacting identical particles (they do not interact with each other, but may each interact with external potential, V). The total Hamiltonian is the sum of those for each particle (same as in classical mechanics):

$$H = \sum_i h_i = \sum_i \left(\frac{p_i^2}{2m} + V(r_i) \right). \tag{1}$$

If $\psi_a(r)$ is a solution to $h\psi_a = \varepsilon_a \psi_a$ (similarly for ψ_b), then it is clear that

$$\Psi_{ab}(r_1, r_2) = \psi_a(r_1)\psi_b(r_2) \tag{2}$$

is a solution to H, with eigenvalue $(\varepsilon_a + \varepsilon_b)$. So is the "interchanged" solution $\psi_b(r_1)\psi_a(r_2)$ (swapped quantum numbers). In fact, since the two particles are identical, such two solutions are completely indistinguishable. Since the solution must of course return to its original state after two interchanges of particles a and b, a sensible general solution can be written,

$$\Psi_{ab}(r_1, r_2) = \frac{1}{\sqrt{2}} \left[\psi_a(r_1)\psi_b(r_2) \pm \psi_b(r_1)\psi_a(r_2) \right]. \tag{3}$$

Without going into the details, it turns out that for Fermions (1/2-integer spin particles, such as electrons), the total wavefunction must be *anti-symmetric* under the exchange of any two particles:

$$\Psi_{ab}(r_1, r_2)^{\text{Fermion}} = \frac{1}{\sqrt{2}} \left[\psi_a(r_1)\psi_b(r_2) - \psi_b(r_1)\psi_a(r_2) \right], \tag{4}$$

[1]J. J. Sakurai, Modern Quantum Mechanics (2011) [in particular Chapters 3, 5, 7]

[2]W. R. Johnson, Atomic Structure Theory (2007)

[3]I. I. Sobelman, Atomic Spectra and Radiative Transitions (1992)

[4]H. A. Bethe and E. E. Salpeter, Quantum Mechanics of One-and Two-Electron Atoms (1977)

[5]J. J. Sakurai, Modern Quantum Mechanics (2011)

while for Bosons (integer spin particles) the total wavefunction must be *symmetric* under the exchange

$$\Psi_{ab}(r_1, r_2)^{\text{Boson}} = \frac{1}{\sqrt{2}} \left[\psi_a(r_1)\psi_b(r_2) + \psi_b(r_1)\psi_a(r_2) \right]. \tag{5}$$

This is to ensure Fermions obey the Fermi-Dirac statistics, and Bosons obey the Bose-Einstein statistics. Note that the anti-symmetry of Fermion wavefunctions encodes the Pauli exclusion principle (spin-statistics theorem).

The same general form applies for systems of many particles. So long as the system is non-interacting, the total wavefunction for fermions/boson can be built of anti-symmetric/symmetric combinations of single-particle wavefunctions.

3.1.2   Slater determinant

For many-Fermion systems (assuming them to be non-interacting), we can form wavefunctions as above, but we must ensure those wavefunctions are properly anti-symmetric under exchange. A nice notational trick to do this is to write the wavefunctions as determinant, called Slater determinants, of the form:

$$\Psi_{ab...n}(r_1, r_2, ..., r_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_a(r_1) & \psi_a(r_2) & \dots & \psi_a(r_N) \\ \psi_b(r_1) & \psi_b(r_2) & \dots & \psi_b(r_N) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_n(r_1) & \psi_n(r_2) & \dots & \psi_n(r_N) \end{vmatrix}, \tag{6}$$

which is an eigenstate of the total Hamiltonian $H = \sum_i^N h(r_i)$. It's simple to see this is equivalent to the two-Fermion case [Eq. (4)]; you should play around with this until you convince yourself it works for the many-Fermion case too. To avoid notation confusion, note that each r_i is a different coordinate variable (not a specific point on the coordinate grid).

Note that, due to the properties of the determinant, interchanging any two columns (corresponding to swapping a pair of quantum numbers) results in a factor of -1, encoding the Fermion anti-symmetry. Also, if any two column are identical, the determinant vanishes, encoding the Pauli exclusion principal.

3.1.3   Matrix elements of multi-Fermion wavefunctions

In practical problems, we often need to evaluate matrix elements of many-particle operators between Slater-determinant wavefunctions.

Let F and G be general one- and two-particle operators

$$\hat{F} = \sum_i \hat{f}(\boldsymbol{r}_i) \quad , \qquad \hat{G} = \frac{1}{2} \sum_{i,j} \hat{g}(\boldsymbol{r}_i, \boldsymbol{r}_j) = \sum_{i<j} \hat{g}(\boldsymbol{r}_i, \boldsymbol{r}_j), \tag{7}$$

where $f(\boldsymbol{r}_i)$ acts on the ith particle; $g(\boldsymbol{r}_i, \boldsymbol{r}_j)$ acts on the pair of particles $\{i, j\}$. The sum extends over each of the N electrons i (or each pair of electrons i, j; the $i < j$ ensures pairs are not double-counted). In regular quantum electrodynamics, this is all that is needed; there are no three-body operators. An example of a one-body operator would be the interaction between an electron and an external field, while an example of a two-body operator is the Coulomb interaction between two electrons.

It is fairly straight-forward, though a little cumbersome, to derive the formulas for calculating matrix elements between many-body Slater-determinant wavefunctions. If you do, you will start to see patterns, which will turn into general rules. I will not prove the rules here, but just state them; they are easy to verify for two-particle wavefunctions.
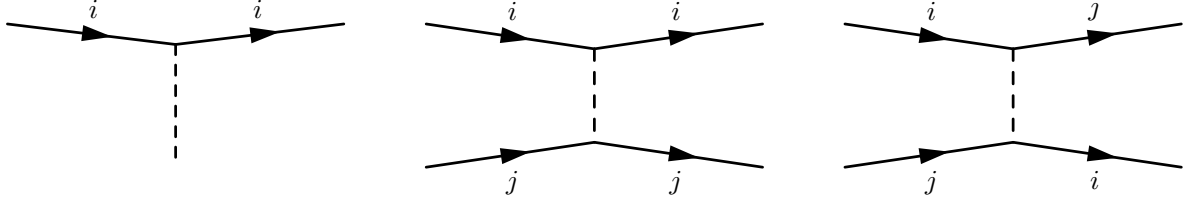
Figure 1: Diagrams representing interaction of single-particle operator with Fermion (left), the direct part of a two-body operator (middle), and exchange (right). Dashed line represents source of interaction.

For diagonal matrix elements (expectation values; initial state = final state):

$$\langle\Psi|F|\Psi\rangle = \sum_i \langle i|f|i\rangle$$
$$\langle\Psi|G|\Psi\rangle = \sum_{i<j} \left(\langle ij|g|ij\rangle - \langle ji|g|ij\rangle\right). \tag{8}$$

Diagrams representing these are shown in Fig. 1. Here, the Dirac notation refers to the single-particle wavefunctions: $|a\rangle = \psi_a$, $|ab\rangle = \psi_a(r_1)\psi_b(r_2)$, meaning

$$\langle a|\hat{h}|b\rangle = \int \psi_a^\dagger \, \hat{h} \, \psi_b \, dV$$
$$\langle ab|\hat{h}|cd\rangle = \iint \psi_a^\dagger(r_1) \, \psi_b^\dagger(r_2) \, \hat{h} \, \psi_c(r_1)\psi_d(r_2) \, dV_1 dV_2. \tag{9}$$

For non-diagonal matrix elements (transitions), the rules are similar. Using a short-hand notation[6], we have for matrix elements between wavefunctions that differ by a single state:

$$\langle\Psi_i^n|F|\Psi\rangle = \langle n|f|i\rangle$$
$$\langle\Psi_i^n|G|\Psi\rangle = \sum_j \left(\langle nj|g|ij\rangle - \langle jn|g|ij\rangle\right), \tag{10}$$

and for matrix elements between wavefunctions that differ by two states:

$$\langle\Psi_{ij}^{nm}|F|\Psi\rangle = 0$$
$$\langle\Psi_{ij}^{nm}|G|\Psi\rangle = \langle nm|g|ij\rangle - \langle mn|g|ij\rangle. \tag{11}$$

3.2 Multi-electron atoms

3.2.1 Mean-field (independent particle) model

We can use the above mechanisms to study the quantum mechanics of many-electron atoms. The total atomic Hamiltonian (in atomic units) is:

$$H = \sum_i^N \left(\frac{\boldsymbol{p}_i^2}{2} - \frac{Z}{|r_i|}\right) + \sum_{i<j} \frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|}. \tag{12}$$

The last term is the electron-electron repulsion term, which includes a sum over every pair of electrons (the $i < j$ ensures pairs are not double-counted).

---

[6]Here, I use a short-hand notation $|\Psi_a^n\rangle = a_n^\dagger a_a|\Psi\rangle$, ($a^\dagger$ and a are creation and annihilation operators) meaning that one particle in state a is replaced by one in state n. e.g., if Ψ is a 3-particle wavefunction with particles in states a, b, c, then Ψ_a^n has particles in states n, b, c. By "state" I mean a given full set of quantum numbers (e.g., n, l, m).

- Clearly, this is *not* a non-interacting system. So how can we use the above formalism?

First, re-write the Hamiltonian as

$$H = \sum_i^N \left(\frac{\boldsymbol{p}_i^2}{2} - \frac{Z}{|r_i|} + u^{\mathrm{MF}}(r_i) \right) + \delta V, \tag{13}$$

where

$$\delta V = \sum_{i<j} \frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} - \sum_i u^{\mathrm{MF}}(r_i). \tag{14}$$

Here, u^{MF} is an (as-of-yet undetermined) potential, which is taken to be roughly the *average* electron-electron interaction term – called the *mean field*. If it is chosen wisely, then δV should be small, and can therefore be treated perturbatively. The physical justification for this approximation is clear – for a system of large number of interacting particles, the individual interactions between all pairs of particles will average out, and the average interaction potential seen by each particle will be essentially the same.

We therefore first solve the *mean field* Hamiltonian with $H \approx H^{\mathrm{MF}}$

$$H^{\mathrm{MF}} = \sum_i^N \left(\frac{\boldsymbol{p}_i^2}{2} - \frac{Z}{|r_i|} + u^{\mathrm{MF}}(r_i) \right), \tag{15}$$

which now *can* be treated as a non-interacting system. Then, we can deal with the remaining δV term later, using perturbation theory: $H = H^{\mathrm{MF}} + \delta V$. This is called the mean-field approximation, or the independent particle picture.

This means we form total (approximate) many-electron wavefunction, Ψ, which satisfies

$$H^{\mathrm{MF}}\Psi = E\Psi, \tag{16}$$

from Slater determinants made from single-electron solutions to the single-particle equation:

$$h\psi = \varepsilon\psi, \tag{17}$$

$$h = \frac{\boldsymbol{p}^2}{2} - \frac{Z}{|r|} + u^{\mathrm{MF}}. \tag{18}$$

In practical calculations, we just calculate and store the set of single-particle solutions, ψ, and use the rules from Sec. 3.1.3 to perform many-body calculations. Importantly, as can be deduced from these rules, the single-particle energies ε, correspond to the binding energies (negative of the ionisation energies) for the individual electrons in the atom.

3.2.2   Initial choice for mean-field

There are many ways to choose a good starting approximation for u^{MF}; here we will discuss a very simple approach. The atomic potential seen by an electron at very small r is essentially unscreened by other electrons. So, in this region, we have $V(r) \approx -Z/r$. Similarly, at very large r there is total screening by the $(Z-1)$ other electrons, so $V(r) \approx -1/r$; see Fig. 2. As a very rough first guess for the mean-field potential, we can chose a smooth potential that connects these two regions. A simple choice is to use a parametric potential; one that works reasonably well is the Green potential

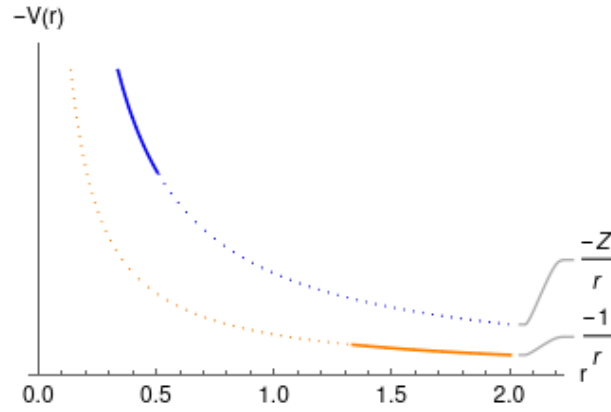$$V_{\mathrm{Gr}}(r) = \frac{(Z-1)}{r} \frac{h\left(e^{r/d} - 1\right)}{1 + h\left(e^{r/d} - 1\right)}, \tag{19}$$

Figure 2: Total atomic potential seen by electron at very small r is essentially unscreened by other electrons, $V(r) \approx -Z/r$, while at very large r there is total screening by the $(Z-1)$ other electrons, $V(r) \approx -1/r$.

where h and d are parameters, which may be tuned to give reasonable results. Note that $V_{\text{nuc}}(r) + V_{\text{Gr}}(r)$ behaves like $-Z/r$ for small r, and $-1/r$ for large r.

Before modern computers this was essentially the best one could do. Now, we can do much better. However, we will use this Green's potential as a starting point, and improve upon it using perturbation theory and the Hartree-Fock routine.

3.3 Many-body perturbation theory (first-order)

3.3.1 Single-valence systems

We will firstly focus on atoms that have a single valence electron above closed-shell core; these are the simplest of the many-electron atoms. All the electrons, besides one, are in "full" shells (each l and m occupied for each n) – this is called the core. The single valence electron lies in an n shell above the core. Due to the energy scaling $\sim 1/n^2$, the energy required to excite a electron from the core is much much larger than that required to excite the valence electron. Therefore, for single-valence systems, the "core" configuration typically remains always the same, while all atomic dynamics are due to the single valence electron. Also, since the valence electron wavefunction is mostly located at larger radius, the single-particle core wavefunctions depends only very little on the influence of the valence electron. From the rules presented in Sec. 3.1.3, all these greatly simplify the calculations.

The single-particle energy of the valence electron can be identified as (approximately) the binding energy of this electron. Therefore, differences in the single-particle energies of different valence states correspond to the transition energies between atoms in those valence states; see Sec. 3.2.1.

3.3.2 First-order perturbation correction to energies

From before, the perturbation to the total Hamiltonian we must consider is:

$$\delta V = \sum_{i<j} \frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} - \sum_i u^{\text{MF}}(r_i), \tag{20}$$

$$\equiv V_{\text{ee}} - U. \tag{21}$$

(second line just defines notation V_{ee} and U, which include the summations). Just as in regular quantum mechanics, the first-order correction to the total atomic energy is thus

$$\delta E = \langle \Psi | V_{\text{ee}} | \Psi \rangle - \langle \Psi | U | \Psi \rangle. \tag{22}$$

To evaluate each of these terms, we must use the rules from Sec. 3.1.3.

The U part is simple, since these are single-particle operators (depend on single electron coordinate only). Using Eq. (8):

$$\langle\Psi|U|\Psi\rangle = \sum_i \langle i|u^{\mathrm{MF}}|i\rangle, \tag{23}$$

where the sum runs over atomic electrons. Note the sum extends over all electrons, and therefore includes summation over all n, l, m and spin quantum numbers. For single-valence atoms, we can break this into the core and valence parts:

$$\langle\Psi|U|\Psi\rangle = \sum_c^{\mathrm{core}} \langle c|u^{\mathrm{MF}}|c\rangle + \langle v|u^{\mathrm{MF}}|v\rangle, \tag{24}$$

where v denotes the state of the valence electron. Notice that the first part, the sum over the core electrons, is the same for any valence state (it is just the correction to core energy). Since all we can observe in experiments is the energy for transitions, and for single-valence atoms the core essentially remains the same, we can drop this part (it will cancel in transitions) – i.e., it does not contribute to transition energies between valence states, or therefore to the binding/ionisation energy of valence electron.

The V_{ee} part is more complicated, since these are two-particle operators. From Sec. 3.1.3, we arrive at

$$\langle\Psi|V_{\mathrm{ee}}|\Psi\rangle = \sum_{i<j} \left[\langle ij|r_{12}^{-1}|ij\rangle - \langle ij|r_{12}^{-1}|ji\rangle \right] \tag{25}$$

where

$$r_{12}^{-1} \equiv \frac{1}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|}.$$

The first term is known as the *direct* contribution, and the second is called *exchange*. Again, we may separate this into terms involving only core states, and those with core and valence states:

$$\langle\Psi|V_{\mathrm{ee}}|\Psi\rangle = \sum_{a<c}^{\mathrm{core}} \left[\langle ca|r_{12}^{-1}|ca\rangle - \langle ca|r_{12}^{-1}|ac\rangle \right] + \sum_c^{\mathrm{core}} \left[\langle cv|r_{12}^{-1}|cv\rangle - \langle cv|r_{12}^{-1}|vc\rangle \right]. \tag{26}$$

Again, the core part is the same for all valence states, and will thus cancel in transition and ionisation energies for valence states.

Therefore, the first-order perturbation theory correction to the binding energy for valence state v is

$$\delta\varepsilon_v = \sum_c^{\mathrm{core}} \left[\langle cv|r_{12}^{-1}|cv\rangle - \langle cv|r_{12}^{-1}|vc\rangle \right] - \langle v|u^{\mathrm{MF}}|v\rangle. \tag{27}$$

3.3.3   Evaluation of Coulomb integrals

Perturbation theory requires us to evaluate integrals of the form $\langle ab|r_{12}^{-1}|cd\rangle$, which correspond to the Coulomb interaction between electrons. As a reminder, writing the integral explicitly, this means:

$$\langle ab|r_{12}^{-1}|cd\rangle = \iint \psi_a^\dagger(\boldsymbol{r}_1)\psi_b^\dagger(\boldsymbol{r}_2) \frac{1}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} \psi_c(\boldsymbol{r}_1)\psi_d(\boldsymbol{r}_2)\, \mathrm{d}^3\boldsymbol{r}_1 \mathrm{d}^3\boldsymbol{r}_2. \tag{28}$$

To evaluate this integral, we use the Laplace expansion[7], which you have likely come across before in your electrodynamics course:

$$\frac{1}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} = \sum_{k=0}^{\infty} \frac{r_<^k}{r_>^{k+1}} f, \tag{29}$$

---

[7]J. D. Jackson, Classical Electrodynamics (2001)

where $\mathcal{P}$ is a Legendre polynomial, $r_< \equiv \min(|\boldsymbol{r}_1|, |\boldsymbol{r}_2|)$, $r_> \equiv \max(|\boldsymbol{r}_1|, |\boldsymbol{r}_2|)$, and γ is the angle between $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$, and k is known as the multipolarity. For the spherically symmetric problems of atomic physics, it becomes much easier to re-write this in terms of the spherical harmonics (just using their definition):

$$\frac{1}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} = \sum_{k=0}^{\infty} \frac{4\pi}{2k+1} \frac{r_<^k}{r_>^{k+1}} \sum_{q=-k}^{q} (-1)^q \, Y_{k,-q}(\theta_1, \phi_1) \, Y_{k,q}(\theta_2, \phi_2), \tag{30}$$

thus separating the radial and angular parts in a way that makes calculating integrals with wavefunctions in the form:

$$\psi_{nlm}(\boldsymbol{r}) = \frac{P_{nl}(r)}{r} Y_{lm}(\theta, \phi), \tag{31}$$

simple (remember back to previous lecture).

We get expressions in the form:

$$\langle ab | r_{12}^{-1} | cd \rangle = \sum_{kq} A_{\text{abcd}}^{kq} \, R_{abcd}^k, \tag{32}$$

where A_{abcd}^{kq} is the angular integral, and R_{abcd}^k is the radial integral:

$$A_{\text{abcd}}^{kq} \equiv \frac{4\pi}{2k+1} (-1)^q \iint Y_{l_a m_a}^{\dagger}(\hat{n}_1) Y_{l_b m_b}^{\dagger}(\hat{n}_2) Y_{k,-q}(\hat{n}_1) \, Y_{k,q}(\hat{n}_2) Y_{l_c m_c}(\hat{n}_1) Y_{l_d m_d}(\hat{n}_2) \, \mathrm{d}\Omega_1 \mathrm{d}\Omega_2, \tag{33}$$

$$R_{abcd}^k \equiv \iint P_a(r_1) P_b(r_2) \frac{r_<^k}{r_>^{k+1}} P_c(r_1) P_d(r_2) \, \mathrm{d}r_1 \mathrm{d}r_2. \tag{34}$$

It is convenient to write R_{abcd}^k as

$$R_{abcd}^k = \int_0^{\infty} P_a(r) \, y_{bd}^k(r) \, P_c(r) \, \mathrm{d}r, \tag{35}$$

where y_{bd}^k is called a "Hartree screening function"

$$y_{bd}^k(r) \equiv \int_0^{\infty} P_b(r') \frac{r_<^k}{r_>^{k+1}} P_d(r') \, \mathrm{d}r' \tag{36}$$

$$= \int_0^r P_b(r') \frac{(r')^k}{r^{k+1}} P_d(r') \, \mathrm{d}r' + \int_r^{\infty} P_b(r') \frac{r^k}{(r')^{k+1}} P_d(r') \, \mathrm{d}r'. \tag{37}$$

The angular part of the integral boils down to integrals of spherical harmonics; importantly, it depends only on the angular quantum numbers l and m (and multipolarity k), and not the specific form of the wavefunction. The angular factor can be calculated geometrically by doing the analytic integrals over angular coordinates. In reality, it is much easier to do these integrals algebraically, by making use of the orthogonality properties of the spherical harmonics and the quantum theory of angular momentum. Simple in concept, such calculations are often very complex, and we will not deal with them at all here. For more information, see the textbooks by Johnson[8], or (for the particularly brave) Varshalovich[9].

---

[8] W. R. Johnson, Atomic Structure Theory (2007)

[9] D. A. Varshalovich, A. N. Moskalev, and V. K. Khersonskii, Quantum Theory of Angular Momentum (1988)

3.4   Hartree-Fock – self-consistent field

3.4.1   Hartree-Fock potential

Motivated by the above, we define a potential, which we will call v_{HF} (Hartree-Fock potential), such that

$$\langle a|v_{\mathrm{HF}}|a\rangle = \sum_{i\neq a}\left[\underbrace{\langle ia|r_{12}^{-1}|ia\rangle}_{\text{Direct}} - \underbrace{\langle ia|r_{12}^{-1}|ai\rangle}_{\text{Exchange}}\right]. \tag{38}$$

Note that this is the expectation value of r_{12}^{-1} for the state a – i.e., the average value of the electron-electron repulsion. Therefore, we may use this potential instead of u^{MF} when solving the Schrödinger equation! I will justify this below, but first, lets work out explicit formulas for v_{HF}.

The direct part is easy; we just don't integrate over coordinates for ψ_a;

$$v_{\mathrm{HF}}^{\mathrm{direct}}(\boldsymbol{r}_1) = \sum_{i\neq a}\int \frac{|\psi_i(\boldsymbol{r}_2)|^2}{r_{12}}\,\mathrm{d}^3\boldsymbol{r}_2. \tag{39}$$

The exchange part is more complex, and cannot be written as a local potential. Instead, we have:

$$v_{\mathrm{HF}}^{\mathrm{exch.}}\psi_a(\boldsymbol{r}_1) = -\sum_{i\neq a}\left(\int \frac{\psi_i^\dagger(\boldsymbol{r}_2)\psi_a(\boldsymbol{r}_2)}{r_{12}}\,\mathrm{d}^3\boldsymbol{r}_2\right)\psi_i(\boldsymbol{r}_1). \tag{40}$$

It is fairly easy to check that these formulas agree with Eq. (38) ($v_{\mathrm{HF}} = v_{\mathrm{HF}}^{\mathrm{direct}} + v_{\mathrm{HF}}^{\mathrm{exch.}}$). Notice that, for valence states, the summations simply extend over all core electrons.

After performing the angular integrals, and after summing over magnetic quantum numbers, we can present the effective direct potential that enters the *radial* Schrödinger equation.

$$v^{\mathrm{direct}}P_v(r) = \sum_{n_c l_c}^{\mathrm{core}} 2(2l_c + 1)\, y_{cc}^0(r)\, P_v(r), \tag{41}$$

where the sum extends over just the principle and orbital angular momentum quantum numbers for the electrons in the core, and y^0 is given by Eq. (36). Only the $k = 0$ term from the Laplace expansion survives in the direct part. The angular part of the exchange term is a little more complicated, and requires some theory we have not yet covered. Notice that the $(2l + 1)$ is simply the number of electrons in that shell ($m = -l, ..., l$), with the extra factor of 2 accounting for spin.

There is a second way to derive the direct part of the potential, which further justifies its use as a potential in the Schrödinger equation. Consider the electrostatic potential seen by an electron, a, due to the other $Z - 1$ other electrons in an atom. This is due to the electric charge density of the electron cloud, call it $\rho(r)$. Now, we know that this is just the same as the electron probability density, times the electron charge:

$$\rho(r) = e\sum_{i\neq a}|\psi_i(r)|^2.$$

We can use Gauss' law to work out what the electrostatic potential due to this charge density is; it will not be a surprise that we get exactly back the direct part of the potential, Eq. (39).

3.4.2   Exchange potential

As stated above, the exchange potential is more complicated, since it cannot be written as a function of one coordinate. Instead, we typically define its action on a state. In terms of the radial wavefunction, P, (i.e., after angular integrations and summation over magnetic quantum numbers and spin),

it can be shown to be:

$$v^{\text{exch}} P_a(r) = -\sum_c^{\text{core}} 2(2l_c + 1) \sum_k \Lambda^k_{l_a,l_c} \, y^k_{ca}(r) \, P_c(r), \tag{42}$$

where Λ is the angular coefficient. Note that it is the *core state*, P_c, appears directly in the right-hand side. The state a appears inside the y^k Coulomb integral. This is due to the "exchange" nature of the interaction (particles a and c have exchanged).

The full expression for Λ is:

$$\Lambda^k_{ab} = \frac{1}{2} \begin{pmatrix} l_a & k & l_b \\ 0 & 0 & 0 \end{pmatrix}^2, \tag{43}$$

where (:::) is called a $3j$-symbol (related to Clebsch-Gordan coefficients). It turns out that Λ is symmetric under any interchange of a,b,k. If we only consider s ($l = 0$) and p ($l = 1$) states, then the only non-zero Λ coefficients are:

$$\Lambda^0_{00} = \frac{1}{2}, \qquad \Lambda^1_{01} = \Lambda^0_{11} = \frac{1}{6}, \qquad \Lambda^2_{11} = \frac{1}{15}. \tag{44}$$

3.4.3   Self-consistent field method

In the previous section we derived the Hartree-Fock potential, which we hope to use in place of the mean-field potential u^{MF} when solving the Schrödinger equation to determine the wavefunctions. However, the Hartree-Fock potential itself depends on the wavefunctions! Therefore, we must start with an initial "guess" for the wavefunctions, and iteratively improve our approximation.

- Use initial approximation for u^{MF} (e.g., Green potential), solve Schrödinger equation to generate set of single-electron wavefunctions

- Use these wavefunctions to form v^{HF}, which is a better potential than the initial approximation

- Use this better potential to generate a set of better wavefunctions

- Now that we have a better set of wavefunctions, can form a better-yet potential, and so-on

- We continue this procedure iteratively, until the solutions converge.

The physical justification for this procedure is simple; the inter-electronic potential depends on the distribution of atomic electrons. By continuously improving the model for the electron wavefunctions, we will improve our model for the inter-electronic potential, which will improve our resulting wavefunctions and so on.

That this method is an accurate approximation can be proven by considering the first-order perturbation theory correction to the energy, when v^{HF} was used as the potential in the Schrödinger equation. In fact, due to the very definition of the Hartree-Fock potential, it is a simple matter to see that this is exactly zero! Therefore, there are no first-order corrections to energies (or, indeed, to the wavefunctions) when the Hartree-Fock potential is used. In order to improve the accuracy further, we must consider higher-order perturbation theory corrections, which become much more complicated, and is an active area of current research (honours/PhD projects available!).