3 Atomic physics – multi-electron atoms

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 Basis of single-electron wavefunctions ("orbitals")

Here we briefly review another method for solving the radial Schrödinger equation that is particularly useful for multi-electron atoms. As we shall see below, the total wavefunction for a multi-electron atom is formed from combinations of single-particle wavefunctions (which we often refer to as "orbitals", though that term is used differently in many sources).

3.1.1 Algebraic solution to radial equation

Use some (finite) set of basis functions $\{b_i(r)\}$, and write:

$$P(r) = \sum_i c_i b_i(r). \tag{1}$$

In general, this is approximate, since the basis set is finite. As such, a good choice of basis is essential; this will be discussed below. Remember that here $P(r)$ is defined via the radial decomposition for the single-particle wavefunctions

$$\psi_{nlm}(\boldsymbol{r}) = \frac{P_{nl}(r)}{r} Y_{lm}(\theta, \phi), \tag{2}$$

and is a solution to the *radial* Schrödinger equation:

$$HP = \varepsilon P. \tag{3}$$

Solving this equation is cast to determining the expansion coefficients $\{c_i\}$. Note: in general, the basis states $|b_j\rangle$ are orthogonal or normalised, and they are not eigenstates of the Hamiltonian.

Using Dirac notation with $|i\rangle = b_i$, this gives:

$$\sum_i H|b_i\rangle c_i = \varepsilon \sum_j |b_j\rangle c_j \tag{4}$$

$$\sum_i \langle b_j|H|b_i\rangle c_i = \varepsilon \sum_i \langle b_k|b_i\rangle c_i, \tag{5}$$

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[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)

where we multiplied on the left by $\langle b_j|$ (and integrated). The result is just a matrix equation:

$$\sum_i H_{ji}c_i = \varepsilon \sum_i B_{ji}c_i \tag{6}$$

$$\implies \quad H\boldsymbol{c} = \varepsilon B\boldsymbol{c}. \tag{7}$$

This is a generalised eigenvalue matrix equation, which can be solved to yield a set of eigenvalues ε, and eigen vectors $\boldsymbol{c}$. Each eigenvector is the set of c_i expansion coefficients. Note that if the basis set if orthonormal, the S matrix $B_{ij} = \langle b_i|b_j\rangle$ is just the identity; however, this is not true in general. The Fortran routine, DSYGV, will solve the generalised eigenvalue problem for real, symmetric matrices. (DSYGV is similar to DSYEV, but takes in also second matrix, B.)

Here, H and B are $N_b \times N_b$ square matrices, with elements:

$$H_{ij} = \langle i|\hat{H}|j\rangle = \int b_i(r)\hat{H}b_j(r)\,\mathrm{d}r\,, \qquad B_{ij} = \langle i|j\rangle = \int b_i(r)b_j(r)\,\mathrm{d}r, \tag{8}$$

with N_b being the number of basis states (B-splines) used the the expansion (1) – not the number of radial grid-points used for integrals. If the basis was orthonormal, S would just be the identity matrix; in general it is not.

For the general case of $H = -\frac{1}{2}\frac{\partial^2}{\partial r^2} + V(r)$, we have

$$H_{ij} = -\frac{1}{2}\int b_i(r)b_j''(r)\,\mathrm{d}r + \int b_i(r)V(r)b_j(r)\,\mathrm{d}r \tag{9}$$

$$= +\frac{1}{2}\int b_i'(r)b_j'(r)\,\mathrm{d}r + \int b_i(r)V(r)b_j(r)\,\mathrm{d}r \tag{10}$$

(integration by parts). In theory, these integrals can be found with extremely high accuracy using Gaussian quadrature. For our purposes, any reasonable integration scheme will do just fine.

Example 3.1: `DSYGV` Parameters. Documentation: http://www.netlib.org/lapack/explore-html/index.html.

```
extern "C"
int dsygv_(
    int *ITYPE,   // =1 for problems of type Av=eBv
    char *JOBZ,   // ='V' means calculate eigenvectors
    char *UPLO,   // 'U': upper triangle of matrix is stored, 'L': lower
    int *N,       // dimension of matrix A
    double *A,    // c-style array for matrix A (ptr to array, pointer to a[0])
                  // On output, A contains matrix of eigenvectors
    int *LDA,     // For us, LDA=N
    double *B,    // c-style array for matrix B [Av=eBv]
    int *LDB,     // For us, LDB =N
    double *W,    // Array of dimension N - will hold eigenvalues
    double *WORK, // 'workspace': array of dimension LWORK
    int *LWORK,   // dimension of workspace: ~ 6*N works well
    int *INFO     // error code: 0=worked.
);
```

- Note: FORTRAN (language LAPACK is written in) uses column-major ordering to access 2D arrays, wile c and c++ use row-major. This means m[i][j] in c++ is m[j][i] in FORTRAN.. so we often need to transpose the matrix before sending to LAPACK
    - Our matrix is symmetric, so this doesn't matter, except for ‘uplo’

  - 'uplo': 'U' means upper triangle in FORTRAN is stored – so lower in c++ [you may just fill entire matrix]
  - For other LAPACK functions, you can often just tell them the matrix is a transpose, so we don't need to waste time transposing it ourselves

- Don't forget to declare the 'dsygv_' function with 'extern "C"', and use the -llapack linker (compile) flag (you may also need the -lblas flag)

3.1.2 B-spline basis functions

There are many options for which set of basis functions to use in Eq. (1). One option that works very well for atomic physics is to use "B-splines".

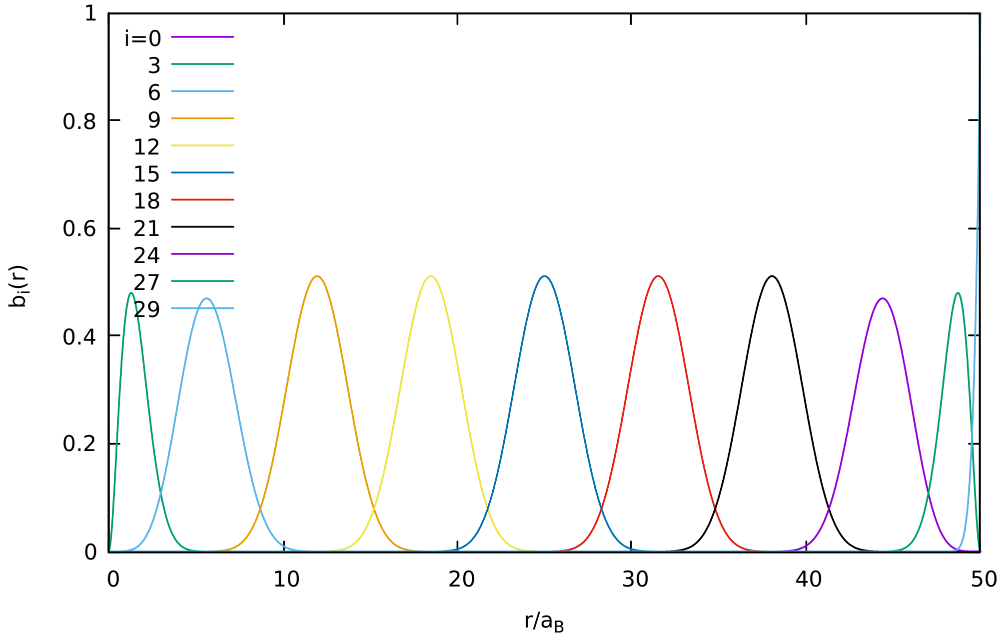

Figure 1: Every 3rd spline from a set of 30 B-splines of order $k = 7$ defined on $r \in [0, 50]$ a.u. The first non-zero knot was placed at $r_0 = 10^{-3}$ a.u., and the knots where distributed uniformly over $[r_0, R]$ (though it is typical to instead distribute them logarithmically).

B-splines are are a set of N piecewise polynomials of order k, defined over a sub-domain $r \in [0, R]$.

- Each spline function, b_i, is non-zero for only a small sub-region of the domain.
  - Technical details (you don't need to know):
  - $b_i(r)$ in non-zero only for $t_i \leq r < t_{i+n}$, where $\{t_0, \ldots, t_N\}$ are a series of $N+1$ "knots".
  - First k knots are placed at $r = 0$; the final k knots are at $r = R$; the remaining knots are distributed between some non-zero r_0 and R.

- All splines go to zero at $r = 0$, except the 0th spline (index 0); the 0th spline (index 0) is only non-zero for $r < r_0$

- The kth spline and above [index k] are non-zero only for $r > r_0$

- All splines go to zero at $r = R$, except for the final one $(N-1)$th spline

- For any $r \in [0, R]$, $\sum_i b_i(r) = 1$
- Form a complete basis for any polynomial of order k on interval $r \in [0, R]$
- Typically, we choose $r_0 \sim 10^{-4}$ a.u., $R \sim 30 - 75$ a.u., $N = 30 - 100$, and $k = 7 - 9$.

3.1.3 Enforce boundary conditions

There are several ways to enforce the boundary conditions, including adding extra fictitious infinite potentials to the Hamiltonian at $r = 0$ and $r = R$. We will take a simpler approach, and enforce the boundary conditions by discarding some of the splines.

- Discard b_0 – this is the only spline non-zero at $r = 0$, forcing wavefunctions to be $P(0) = 0$
- Discard final spline b_{N-1} – this is the only spline non-zero at $r = R$, forcing wavefunctions to be $P(R) = 0$ ("hard" boundary condition)
- Discard b_1 – We can further take advantage of low-r behaviour of the wavefunctions; $P(r) \sim r^{l+1}$. Due to form of the splines, we can force this behaviour by discarding b_1 for s and p states.
- So, with N total splines, we actually use only $N - 3$ in the expansion Eq. (1).

3.2 Many-particle quantum mechanics

3.2.1 Exchange symmetry, product states

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):

$$H = \sum_i h_i = \sum_i \left(\frac{p_i^2}{2m} + V(r_i) \right). \tag{11}$$

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

$$\Psi_{ab}(r_1, r_2) = \psi_a(r_1)\psi_b(r_2) \tag{12}$$

is also 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 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,

$$\Psi_{ab}(r_1, r_2) = \frac{1}{\sqrt{2}} \left[\psi_a(r_1)\psi_b(r_2) \pm \psi_b(r_1)\psi_a(r_2) \right]. \tag{13}$$

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

$$\Psi_{ab}(r_1, r_2)^{\text{Fermion}} = \frac{1}{\sqrt{2}} \left[\psi_a(r_1)\psi_b(r_2) - \psi_b(r_1)\psi_a(r_2) \right], \tag{14}$$

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

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

$$\Psi_{ab}(r_1,r_2)^{\rm Boson} = \frac{1}{\sqrt{2}}\left[\psi_a(r_1)\psi_b(r_2)+\psi_b(r_1)\psi_a(r_2)\right]. \tag{15}$$

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 can be built of products of single-particle wavefunctions, called product states (or Fock states).

3.2.2 Slater determinant

For many-Fermion systems (assuming them to be non-interacting), we can form wavefunctions using product states, 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:

$$\Psi_{ab\ldots n}(r_1,r_2,...,r_N) = \frac{1}{\sqrt{N!}}\begin{vmatrix}\psi_a(r_1) & \psi_a(r_2) & \ldots & \psi_a(r_N)\\ \psi_b(r_1) & \psi_b(r_2) & \ldots & \psi_b(r_N)\\ \vdots & \vdots & \ddots & \vdots\\ \psi_n(r_1) & \psi_n(r_2) & \ldots & \psi_n(r_N)\end{vmatrix}, \tag{16}$$

which is an eigenstate of the total Hamiltonian $H=\sum_i^N h(r_i)$. To avoid notation confusion, note that each r_i is a different coordinate variable (not a specific point on the coordinate grid). It is easiest to see that this works in the case of $N=2$ Fermions, but works in general.

3.2.3 Matrix elements of multi-Fermion wavefunctions

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

$$\hat{F} = \sum_i \hat{f}(\boldsymbol{r}_i) \quad , \qquad \hat{G} = \sum_{i<j}\hat{g}(\boldsymbol{r}_i,\boldsymbol{r}_j), \tag{17}$$

where $f(\boldsymbol{r}_i)$ acts on the ith particle; $g(\boldsymbol{r}_i,\boldsymbol{r}_j)$ acts on the pair of particle $\{i,j\}$. 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 mechanics, this is all that is needed; there are no three-body operators.

It is fairly straight-forward, though a little cumbersome, to derive the rules 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.

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

$$\begin{aligned}\langle\Psi|F|\Psi\rangle &= \sum_i\langle i|f|i\rangle\\ \langle\Psi|G|\Psi\rangle &= \sum_{i<j}\left(\langle ij|g|ij\rangle - \langle ji|g|ij\rangle\right).\end{aligned} \tag{18}$$

Diagrams representing these are shown in Fig. 2. 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

$$\begin{aligned}\langle a|h|b\rangle &= \int \psi_a^\dagger\, h\,\psi_b\,{\rm d}V\\ \langle ab|h|cd\rangle &= \iint \psi_a^\dagger(r_1)\,\psi_b^\dagger(r_2)\,h\,\psi_c(r_1)\psi_d(r_2)\,{\rm d}V_1{\rm d}V_2.\end{aligned} \tag{19}$$

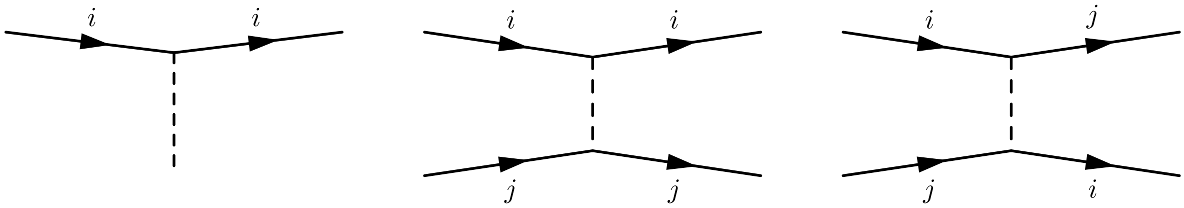

Figure 2: Diagrams representing interaction of single-particle operator with Fermion (left), the direct part of a two-body operator (middle), and exchange (right). Dashed line represents source of interaction.

For 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:

$$\begin{aligned}\langle\Psi_i^n|F|\Psi\rangle &= \langle n|f|i\rangle\\ \langle\Psi_i^n|G|\Psi\rangle &= \sum_j\left(\langle nj|g|ij\rangle - \langle jn|g|ij\rangle\right),\end{aligned}\tag{20}$$

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

$$\begin{aligned}\langle\Psi_{ij}^{nm}|F|\Psi\rangle &= 0\\ \langle\Psi_{ij}^{nm}|G|\Psi\rangle &= \langle nm|g|ij\rangle - \langle mn|g|ij\rangle.\end{aligned}\tag{21}$$

3.3 Multi-electron atoms

3.3.1 Mean-field (independent particle) model

We can use the above mechanisms to study the quantum mechanics of many-electron atoms.

$$H = \sum_i^N\left(\frac{\boldsymbol{p}_i^2}{2} - \frac{Z}{|r_i|}\right) + \sum_{i<j}\frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|}.\tag{22}$$

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).

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

First, re-write the Hamiltonian as

$$H = \sum_i^N\left(\frac{\boldsymbol{p}_i^2}{2} - \frac{Z}{|r_i|} + u^{\rm MF}(r_i)\right) + \delta V,\tag{23}$$

where

$$\delta V = \sum_{i<j}\frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} - \sum_i u^{\rm MF}(r_i).\tag{24}$$

Here, $u^{\rm MF}$ 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 widely, then δV should be small, and can therefore be treated perturbatively. The physical justification for this approximation is

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[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).

clear - for a system of large number of interacting particles, the indevidual 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 $H \approx H^{\rm MF}$

$$H^{\rm MF} = \sum_i^N \left(\frac{\boldsymbol{p}_i^2}{2} - \frac{Z}{|r_i|} + u^{\rm MF}(r_i) \right), \tag{25}$$

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

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

$$H^{\rm MF}\Psi = E\Psi, \tag{26}$$

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

$$h\psi = \varepsilon\psi, \tag{27}$$

$$h = \frac{\boldsymbol{p}^2}{2} - \frac{Z}{|r|} + u^{\rm MF}. \tag{28}$$

In practicle calculations, we just calculate and store the set of single-particle solutions, ψ, and use the rules from Sec. 3.2.3 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.

3.3.2 Initial choice for mean-field

There are many ways to choose a good starting approximation for $u^{\rm MF}$; 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. 3. 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

$$V_{\rm Gr}(r) = \frac{(Z-1)}{r} \frac{h\left(e^{r/d}-1\right)}{1+h\left(e^{r/d}-1\right)}, \tag{29}$$

where h and d are parameters, which may be tuned to give reasonable results. Note that $V_{\rm nuc}(r) + V_{\rm Gr}(r)$ 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.

3.4 Many-body perturbation theory (first-order)

3.4.1 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

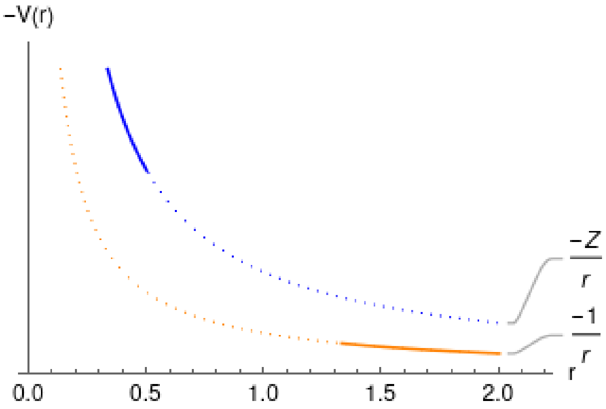

Figure 3: Total atomic potential seen by electron at very small r is essentially unscreened by other electrons, $V(r) \approx -Z/r$, while at very large r there is total screening by the $(Z-1)$ other electrons, $V(r) \approx -1/r$.

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. 3.2.3, 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. 3.3.1.

3.4.2 First-order perturbation correction to energies

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

$$\delta V = \sum_{i<j} \frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} - \sum_i u^{\rm MF}(r_i), \tag{30}$$

$$\equiv V_{\rm ee} - U. \tag{31}$$

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

$$\delta E = \langle \Psi | V_{\rm ee} | \Psi \rangle - \langle \Psi | U | \Psi \rangle. \tag{32}$$

To evaluate each of these terms, we must use the rules from Sec. 3.2.3.

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

$$\langle \Psi | U | \Psi \rangle = \sum_i \langle i | u^{\rm MF} | i \rangle, \tag{33}$$

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:

$$\langle \Psi | U | \Psi \rangle = \sum_c^{\rm core} \langle c | u^{\rm MF} | c \rangle + \langle v | u^{\rm MF} | v \rangle, \tag{34}$$

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 ionisation energy of valence electron.

The $V_{\rm ee}$ part is more complicated, since these are two-particle operators. From Sec. 3.2.3, we arrive at

$$\langle\Psi|V_{\rm ee}|\Psi\rangle = \sum_{i<j}\left[\langle ij|r_{12}^{-1}|ij\rangle - \langle ij|r_{12}^{-1}|ji\rangle\right] \tag{35}$$

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:

$$\langle\Psi|V_{\rm ee}|\Psi\rangle = \sum_{a<c}^{\rm core}\left[\langle ca|r_{12}^{-1}|ca\rangle - \langle ca|r_{12}^{-1}|ac\rangle\right] + \sum_{c}^{\rm core}\left[\langle cv|r_{12}^{-1}|cv\rangle - \langle cv|r_{12}^{-1}|vc\rangle\right]. \tag{36}$$

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 energy for valence state v is

$$\delta\varepsilon_v = \sum_{c}^{\rm core}\Big[\langle cv|r_{12}^{-1}|cv\rangle - \langle cv|r_{12}^{-1}|vc\rangle\Big] - \langle v|u^{\rm MF}|v\rangle. \tag{37}$$

3.4.3 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:

$$\langle ab|r_{12}^{-1}|cd\rangle = \iint \psi_a^\dagger(\boldsymbol{r}_1)\psi_b^\dagger(\boldsymbol{r}_2)\,\frac{1}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|}\psi_c(\boldsymbol{r}_1)\psi_d(\boldsymbol{r}_2)\,{\rm d}^3\boldsymbol{r}_1{\rm d}^3\boldsymbol{r}_2. \tag{38}$$

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

$$\frac{1}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} = \sum_{k=0}^{\infty}\frac{r_<^k}{r_>^{k+1}}\mathcal{P}_k(\cos\gamma), \tag{39}$$

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 $\boldsymbol{r}_2$. For the spherically symmetric problems of atom physics, it becomes much easier to re-write this in terms of the spherical harmonics (just using their definition):

$$\frac{1}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} = \sum_{k=0}^{\infty}\frac{4\pi}{2k+1}\frac{r_<^k}{r_>^{k+1}}\sum_{q=-k}^{q}(-1)^q\,Y_{k,-q}(\theta_1,\phi_1)\,Y_{k,q}(\theta_2,\phi_2), \tag{40}$$

thus separating the radial and angular parts in a way that makes calculating integrals with wavefunctions in the form of Eq. (2) simple. We get expressions in the form:

$$\langle ab|r_{12}^{-1}|cd\rangle = \sum_{kq} C^{k,q}_{\rm angular}\,R^k_{abcd}, \tag{41}$$

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

where $C_{\rm angular}$ is the angular integral, and R^k_{abcd} is the radial integral:

$$R^k_{abcd} \equiv \iint P_a(r_1)P_b(r_2)\,\frac{r_<^k}{r_>^{k+1}}\,P_c(r_1)P_d(r_2)\,{\rm d}r_1{\rm d}r_2, \tag{42}$$

which is convenient to write as

$$R^k_{abcd} = \int_0^\infty P_a(r)\,y^k_{bd}(r)\,P_c(r)\,{\rm d}r, \tag{43}$$

where y^k_{bd} is called a "Hartree screening function"

$$y^k_{bd}(r) \equiv \int_0^\infty P_b(r')\,\frac{r_<^k}{r_>^{k+1}}\,P_d(r')\,{\rm d}r' \tag{44}$$

$$= \int_0^r P_b(r')\,\frac{(r')^k}{r^{k+1}}\,P_d(r')\,{\rm d}r' + \int_r^\infty P_b(r')\,\frac{r^k}{(r')^{k+1}}\,P_d(r')\,{\rm d}r'. \tag{45}$$

The angular part of the integral boils down to integrals of spherical harmonics; note that it depends only on the angular quantum numbers l and m (and multipolarity k and q), 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].

3.5 Hartree-Fock – self-consistent field

3.5.1 Hartree-Fock potential

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

$$\langle a|v_{\rm HF}|a\rangle = \sum_{i\neq a}\Big[\underbrace{\langle ia|r_{12}^{-1}|ia\rangle}_{\text{Direct}} - \underbrace{\langle ia|r_{12}^{-1}|ai\rangle}_{\text{Exchange}}\Big]. \tag{46}$$

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 $u^{\rm MF}$ when solving the Schrödinger equation! I will justify this below, but first, lets work out explicit formulas for $v_{\rm HF}$.

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

$$v_{\rm HF}^{\rm direct}(\boldsymbol{r}_1) = \sum_{i\neq a}\int \frac{|\psi_i(\boldsymbol{r}_2)|^2}{r_{12}}\,{\rm d}^3\boldsymbol{r}_2. \tag{47}$$

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

$$v_{\rm HF}^{\rm exch.}\psi_a(\boldsymbol{r}_1) = -\sum_{i\neq a}\left(\int \frac{\psi_i^\dagger(\boldsymbol{r}_2)\psi_a(\boldsymbol{r}_2)}{r_{12}}\,{\rm d}^3\boldsymbol{r}_2\right)\psi_i(\boldsymbol{r}_1). \tag{48}$$

It is fairly easy to check that these formulas agree with Eq. (46) ($v_{\rm HF} = v_{\rm HF}^{\rm direct} + v_{\rm HF}^{\rm exch.}$). Notice that, for valence states, the summations simply extend over all core electrons.

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[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)

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.

$$v^{\rm direct} P_v(r) = \sum_{n_c l_c}^{\rm core} 2(2l_c + 1)\, y^0_{cc}(r)\, P_v(r), \tag{49}$$

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. (44). 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.

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. (47).

3.5.2 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 $u^{\rm MF}$ 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 $u^{\rm MF}$ (e.g., Green potential), solve Schrödinger equation to generate set of single-electron wavefunctions
- Use these wavefunctions to form $v^{\rm HF}$, 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 $v^{\rm HF}$ 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!).