

## 1 Radial Dirac equation (spherical potentials)

The Dirac equation is (e.g., [1])

$$(H_D - \varepsilon)\phi(\mathbf{r}) = 0, \quad (1)$$

where  $H_D$  is the Dirac Hamiltonian:

$$H_D = c\boldsymbol{\alpha} \cdot \mathbf{p} + c^2(\beta - 1) + \hat{V}, \quad (2)$$

and  $\boldsymbol{\alpha} = \gamma^0\boldsymbol{\gamma}$  and  $\beta = \gamma^0$  are Dirac matrices. Note that we have subtracted the electron rest energy, so the total relativistic energy is  $E = \varepsilon + c^2$  (for positive total energy/electron states). For bound states,  $\phi \rightarrow 0$  as  $r \rightarrow \infty$  and  $\phi$  is regular everywhere and thus normalisable. The set of solutions  $\{\phi_i\}$  (including the negative energy/positron states) to (1) form a complete orthogonal set/basis. We use the standard normalisation choice, so that  $\langle \phi_i | \phi_j \rangle = \delta_{ij}$ .

For spherically symmetric potentials, we can express the four-component orbitals in the form<sup>1,2</sup>:

$$\phi_{n\kappa m}(\mathbf{r}) = \frac{1}{r} \begin{pmatrix} f_{n\kappa}(r) \Omega_{\kappa m}(\mathbf{n}) \\ ig_{n\kappa}(r) \Omega_{-\kappa, m}(\mathbf{n}) \end{pmatrix}, \quad (3)$$

where  $\kappa = (l - j)(2j + 1)$  is the Dirac quantum number, and  $\Omega$  is a (two-component) spherical spinor,

$$\Omega_{\kappa m} \equiv \sum_{s_z = \pm 1/2} \langle l, m - s_z, 1/2, s_z | j, m \rangle Y_{l, m - s_z}(\mathbf{n}) \chi_{s_z}, \quad (4)$$

with  $\langle j_1 m_1 j_2 m_2 | JM \rangle$  a Clebsch-Gordon coefficient,  $Y_{lm}$  a spherical harmonic,  $\mathbf{n} = \mathbf{r}/r$ , and  $\chi_{s_z}$  is a spin eigenstate [ $\chi_{1/2} = (1, 0)^T$ ,  $\chi_{-1/2} = (0, 1)^T$ ]. The components of  $\phi$  are orthonormal according to the rules:

$$\langle n\kappa | n'\kappa \rangle \equiv \int (f_{n\kappa} f_{n'\kappa} + g_{n\kappa} g_{n'\kappa}) dr = \delta_{n'n} \quad (5)$$

$$\langle \kappa m | \kappa' m' \rangle \equiv \int (\Omega_{\kappa m}^\dagger \Omega_{\kappa' m'}) d\Omega = \delta_{\kappa'\kappa} \delta_{m'm}. \quad (6)$$

In this case, we can define the radial Dirac equation (a pair of coupled first-order ODEs):

$$(H_r - \varepsilon) F_{n\kappa} = 0, \quad (7)$$

where we defined the “radial spinor”

$$F_{n\kappa} = \begin{pmatrix} f_{n\kappa}(r) \\ g_{n\kappa}(r) \end{pmatrix}, \quad (8)$$

and “radial Hamiltonian”

$$H_r = \begin{pmatrix} \hat{V} & c(\frac{\kappa}{r} - \partial_r) \\ c(\frac{\kappa}{r} + \partial_r) & \hat{V} - 2c^2 \end{pmatrix}. \quad (9)$$

Note that the 3D Hamiltonian can also be expressed in this form simply by replacing  $\kappa$  in (9) with  $-\hat{k}$  (top right) and  $\hat{k}$  (bottom left), where  $\hat{k} \equiv -1 - \boldsymbol{\sigma} \cdot \mathbf{l}$ , and  $\hat{k}\Omega_{\kappa m} = \kappa\Omega_{\kappa m}$ . I will suppress the  $r$  subscript and use  $(H - \varepsilon)F = 0$  and  $(H - \varepsilon)\phi = 0$  interchangeably, since there is no risk of confusion. Equation (7) is often written in the equivalent form:

$$\begin{aligned} (\hat{V} - \varepsilon) f - c \left( g' - \frac{\kappa}{r} g \right) &= 0, \\ (\hat{V} - 2c^2 - \varepsilon) g + c \left( f' + \frac{\kappa}{r} f \right) &= 0. \end{aligned} \quad (10)$$

### 1.1 Nuclear and electron potentials

For a many-electron atom, the potential term consists of the sum of the nuclear and inter-electron potentials:

$$\hat{V} = V_{\text{nuc}} + V_{\text{el}}. \quad (11)$$

The electron potential,

$$V_{\text{el}} = \sum_{i < j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}, \quad (12)$$

involves a huge number of terms and must be taken into account approximately. The methods used to approximate this term will be described in the following sections. For a point-like nucleus,  $V_{\text{nuc}} = -Z/r$ ; in reality, the nuclear charge is distributed across the finite-size nucleus, and this must be taken into account.

To form  $V_{\text{nuc}}$ , we assume the nuclear charge is distributed according to a Fermi distribution,

$$\rho(r) = \rho_0 (1 + \exp[(r - c)/a])^{-1}, \quad (13)$$

where  $\rho_0$  is the normalisation factor, ( $\int \rho dV = Z$ ),  $c$  is the half-density radius, and  $a$  is defined via the 90–10% density fall-off  $t \equiv 4a \ln 3$  (known as the “skin thickness”), which we take to be  $t = 2.3$  fm for all isotopes. The half-density radius is related to  $a$  and  $r_{\text{rms}}$ , the root-mean-square charge radius, as  $c = \sqrt{(5r_{\text{rms}}^2 - 7\pi^2 a^2)/3}$ . Then,  $V_{\text{nuc}}$  is obtained numerically from (13) using Gauss’ law.

The code also allows you to assume a spherical nucleus:

$$V_{\text{nuc}}^{\text{sphere}}(r) = \begin{cases} -Z \frac{3r_{\text{nuc}}^2 - r^2}{2r_{\text{nuc}}^3} & r < r_{\text{nuc}} \\ -Z \frac{1}{r} & r > r_{\text{nuc}} \end{cases} \quad (14)$$

(with  $r_{\text{nuc}} = \sqrt{5/3} r_{\text{rms}}$ ), which is mainly used for testing.

## 2 Numerical solutions to the Dirac equation

### 2.1 Bound-state solution to local Dirac equation

Wavefunctions for many-electron atoms are formed from single-particle orbitals, see, e.g., Ref. [4]. Rearranging Eq. (7), we can express the single-particle radial derivative as:

$$\partial_r F = \frac{1}{c} \begin{pmatrix} -\frac{\kappa}{r} & (\varepsilon - \hat{V} + 2c^2) \\ -(\varepsilon - \hat{V}) & c\frac{\kappa}{r} \end{pmatrix} F, \quad (15)$$

which has the familiar form of an ODE. We solve this equation using a multi-step method. The specific method used (Adams-Moulton method<sup>3</sup>) is described in detail in the textbook Ref. [2].

In general, Eq. (15) will have solutions for any given  $\varepsilon$ . However, we are interested in the specific bound state solutions, in which  $F \rightarrow 0$  as  $r \rightarrow \infty$ , and  $F(0) \neq \infty$ . To solve the bound-state problem, an initial  $\varepsilon$  is guessed, and the DE is solved using the multi-step method. Then, small adjustments are made to  $\varepsilon$  until (a) we have the correct boundary conditions, and (b) we have the correct state ( $n\kappa$ ) determined by the number of nodes of the orbital ( $n - l - 1$ ).

<sup>3</sup>In the code, we can use the method of order 5 to 8 (default is 5; changing makes essentially no difference) – must be set at compile time.

<sup>1</sup>We use the Dirac basis; see Appendix C.

<sup>2</sup>Our notation differs from that appearing in other places; e.g., compared to Ref. [1] we have  $f \leftrightarrow g$ , and compared to [2] we have:  $f_{\text{here}} = P_{\text{Johnson}}$ ,  $g_{\text{here}} = -Q_{\text{Johnson}}$ , and compared to Ref. [3] we have  $g_{\text{here}} = \alpha g_{\text{Dzubau}}$ .

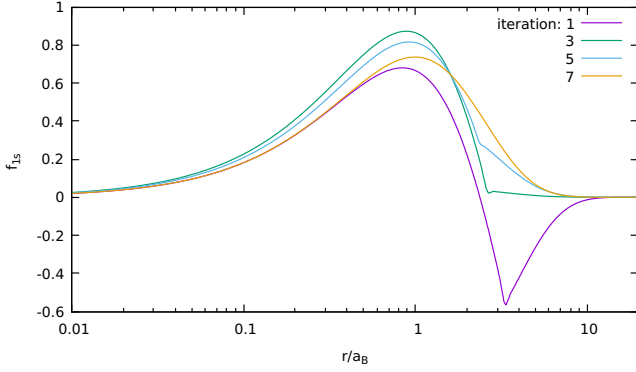


Figure 1: Hydrogen 1s orbital, as calculated at the first through 7th iteration. For this example, the initial energy guess was  $-0.3\text{au}$ , and converged to  $-0.500006566..$  to parts in  $10^{-16}$  in 12 iterations.

In order to use the multi-step method, a few initial points of the radial  $F$  function are required. These are determined by solving the asymptotic form of the Dirac equation analytically accounting for the boundary conditions. It is common to expand the orbital around  $r = 0$  to start the procedure, and then adjust the energy until  $F \rightarrow 0$  at infinity.

A more numerically stable approach, however, is to solve the DE twice, once starting from  $r = 0$ , and once from  $r = \infty$  [2]. These two solutions are stepped inwards toward some central point, where the two solutions are joined – one of the two solutions is re-scaled so that  $f_0 = f_\infty$  at the defined point. Small energy adjustments are made until the lower  $g$  components also match at this point (this ensures the derivatives match, and the join is smooth). In our case, the two solutions are not joined at a single point, but are instead “meshed” across a few ( $\simeq 5$ ) points around the classical turning point, defined via  $V(r_{\text{ctp}}) = \varepsilon$  (this is slightly different from Ref. [2]). The meshing procedure acts to smooth out numerical noise, and makes the method more numerically stable. This procedure typically allows convergence of the energies to parts in  $10^{16}$ ; see Fig. 1 for an example.

Note that Eq. (15) does not determine the normalisation for  $F$ , so the solutions must be normalised explicitly [Eq. (5)]. Further, the sign of  $F$  is also arbitrary from Eq. (15); we choose  $f(r)$  to be positive as  $r \rightarrow 0$ , as is standard.

Everywhere in the code, the fine structure constant is replaced with:  $\alpha \rightarrow \lambda\alpha_0$  (in atomic units,  $\alpha = 1/c$ ), where  $\alpha_0 \approx 1/137$ . The factor  $\lambda$  is a run-time input option, that is 1 by default. For example, letting  $\lambda \rightarrow 0$  (i.e.,  $c \rightarrow \infty$ ) allows us to perform calculations in the non-relativistic limit. This is a particularly useful option for checking the calculations, and for determining the sensitivity of particular observables to variations in the fine structure constant. Modifications can also be made to the above equations to account for the finite electron/nucleus mass (reduced mass) – but this is not implemented in the code.

## 2.2 Radial grid

The equations must be solved numerically on a finite radial grid (the orbitals are stored in arrays on this grid). We define a grid on the region from  $r_0$  to  $r_{\text{max}}$ , that has  $N$  points.

Typically, we do not want to use a uniformly spaced grid,

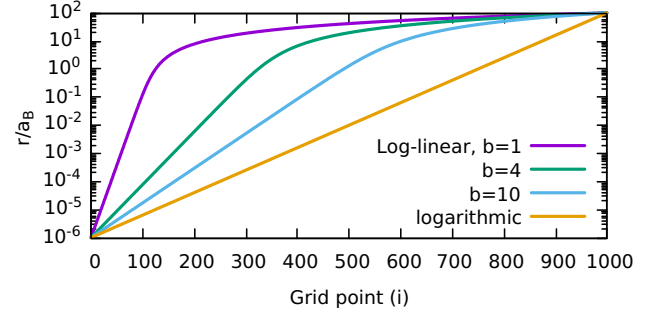


Figure 2: Radial distance  $r_i$  as function of grid-point,  $i$ .

since the wavefunctions vary very rapidly at small distances, but rather slowly at large distances. We define a non-uniformly-spaced radial grid ( $r_i$ ) in terms of a uniformly spaced  $u$  grid ( $u_{i+1} = u_i + \delta u$ ). In this case, integrals become:

$$\int_0^\infty f(r) dr \rightarrow \int_{r_0}^{r_{\text{max}}} f(r) dr \rightarrow \int_{u_0}^{u_{\text{max}}} f(r(u)) \frac{dr}{du} du, \quad (16)$$

which numerically becomes:

$$\int_{u_0}^{u_{\text{max}}} f(r(u)) \frac{dr}{du} du \rightarrow \sum_{i=0}^{N-1} f(r_i) \frac{dr}{du} \Big|_i \delta u \quad (17)$$

(in the code we actually use an  $n$ -point quadrature integration formula for the integrals). The initial/final grid points, and the grid spacings, must be chosen such that the above numerical approximations are sufficiently accurate.

In the code, we can set either a logarithmic grid, defined:

$$u = \ln(r), \quad \frac{dr}{du} = r, \quad (18)$$

or a mixed log-linear grid, defined:

$$u = r + b \ln(r), \quad \frac{dr}{du} = \frac{r}{r + b}, \quad (19)$$

which is approximately logarithmic at small distances ( $r < b$ ), and approximately linear at large distances (typically  $b \simeq 4\text{au}$ ); see Fig. 2. The logarithmic grid works very well, and allows good convergence without requiring a large number of points, but works less well for highly excited states, and works quite poorly for continuum states with high energy. The log-linear grid works well in a wide range of cases, but often needs more grid points to achieve the same numerical accuracy<sup>4</sup>.

## 2.3 Dirac equation involving inhomogeneous or non-local terms (Green’s Method)

This is a brief overview only; for explanations/proofs see, e.g., Ref. [5]. Consider the inhomogeneous Dirac equation, with extra ‘source’ term  $S$ :

$$(H_1 - \varepsilon) F = S, \quad (20)$$

where  $H_1$  is a Dirac Hamiltonian involving only local potential terms. We solve this for a normalisable  $F$  using the Green’s method for ODEs. First, take the homogeneous equation:

$$(H_1 - \varepsilon) G = 0, \quad (21)$$

<sup>4</sup>The code also allows the use of linear grid – but this requires a very large number of points to work, so should only be used for testing.

which we solve (for a given energy  $\varepsilon$ ) using the regular linear ODE multi-step methods from Sec. 2.1. Note that since  $F$  is a normalisable solution to (20)  $G$  will *not* (in general) be a normalisable solution to (21). Instead, we seek two solutions, which are each bound by one of the boundary conditions; i.e., one solution that satisfies the boundary condition at the origin,  $G_0$ , and a second that satisfies that at infinity,  $G_\infty$ . Then, from the Green's method, a solution to (20) can be expressed:

$$F(r) = G_\infty(r) \int_0^r \frac{G_0(r')^T S(r')}{c w(r')} dr' r' + G_0(r) \int_r^\infty \frac{G_\infty(r')^T S(r')}{c w(r')} dr' \quad (22)$$

( $A^T B \equiv f_A f_B + g_A g_B$ ) where the Wronskian,

$$w(r) = f_\infty(r) g_0(r) - f_0(r) g_\infty(r), \quad (23)$$

should be independent of  $r$  [the extra  $c$  factor in the denominator is pulled from the definition of the derivative (15) and can be included in  $w$ ].

Note that this method clearly doesn't work if  $w = 0$ ; worse, the method can be numerically unstable if  $S$  and  $w$  are both small (if  $S$  is too small, it implies the  $G_{0,\infty}$  solutions will be similar, and thus  $w$  will be small).

## 2.4 Continuum orbitals

We are sometimes interested in continuum orbitals that are regular at the origin (see, e.g., Ref. [1]). For continuum orbitals of the desired energy  $\varepsilon > 0$ , we solve using the multi-step method described above, starting from the origin and integrating outwards. Note that we do not have  $\phi_c \rightarrow 0$  at large  $r$ , and continuum orbitals cannot be normalised as above. For most problems, however, we do require normalised orbitals.

We choose energy normalisation [1]:

$$\int_{\varepsilon - \delta\varepsilon}^{\varepsilon + \delta\varepsilon} \langle \varepsilon' \kappa m | \varepsilon \kappa m \rangle d\varepsilon' = 1. \quad (24)$$

This equation can not be used directly. Instead, the orbitals are normalised in analogy with analytic Coulomb (H-like) continuum states. For Coulomb potentials, at large  $r$  we have:

$$f(r) \approx \sqrt{\frac{\alpha}{\pi\beta}} \sin(kr + \dots), \quad (25)$$

with

$$\beta = \sqrt{\frac{\varepsilon}{\varepsilon + 2/\alpha^2}}$$

(other terms in sine function are either constant, or logarithmic in  $r$ ). At large  $r$ , the atomic potential is also Coulomb-like, so we can use (25) to normalise the orbitals by enforcing the amplitude of the sine-like orbitals at large  $r$  to be the same as the H-like case.

To do this, we have to extend the radial grid out to very large distances, often much larger than the normal grid used to solve the bound-state orbitals. The orbital is solved out to large  $r$  until the amplitude/frequency of the oscillations becomes close enough to constant, and then the amplitude is re-scaled to match (25). After solving, the orbital is only kept up until  $r_{\max}$ , since larger distances typically do not contribute to any required radial integrals.

## 3 Hartree-Fock (self-consistent field method)

For any general “self-consistent field method”, we start with an initial approximation for the electronic potential (e.g., Thomas-Fermi potential, or a simple parametric potential), and use this to generate a set of orbitals for the desired subset of atomic electrons (e.g., the core). The total electron density formed from these orbital tells us the electronic charge distribution across the atom, which we use to generate a new electronic potential (Gauss' law). In general, this new potential will be a better approximation for the true electronic potential than the initial guess. Form a new set of orbitals in this better potential, which will therefore be a better set of orbitals, which we use to generate a better-yet guess for the potential and so on, until convergence is reached. At the end, the potential used to form the electron orbitals should be the same as the potential that is formed from the electron orbitals, and is thus self-consistent.

### 3.1 Relativistic Hartree-Fock method

The specific method we use for this is the relativistic Hartree-Fock method, which includes the electron exchange interaction. This section largely follows the detailed explanation from Ref. [2], with a few extensions.

By minimising the many-body energy for the single Slater-determinant electronic wavefunction (see textbook [2] for details), the Hartree-Fock potential can be derived as

$$\hat{V}_{\text{HF}} \phi_a(\mathbf{r}_1) = \sum_{i \neq a}^{N_e} \left( \int \frac{\phi_i^\dagger(\mathbf{r}_2) \phi_i(\mathbf{r}_2)}{|\mathbf{r}_{12}|} d^3 \mathbf{r}_2 \phi_a(\mathbf{r}_1) - \int \frac{\phi_i^\dagger(\mathbf{r}_2) \phi_a(\mathbf{r}_2)}{|\mathbf{r}_{12}|} d^3 \mathbf{r}_2 \phi_i(\mathbf{r}_1) \right), \quad (26)$$

where the sum over  $i$  extends over all occupied electrons  $i = \{n_i, \kappa_i, m_i\}$ . The Coulomb integrals are computed by expanding  $r_{12}^{-1}$  in terms of spherical harmonics (Laplace expansion) – see Appendix A. Integrating over angles, and summing over  $m$  quantum numbers we have:

$$\hat{V}_{\text{HF}} F_a(r) = \left( \sum_b [j_b] x_b y_{bb}^0(r) \right) F_a(r) - \frac{1}{[j_a]} \sum_b \tilde{x}_b^a \sum_k (C_{ab}^k)^2 y_{ab}^k(r) F_b(r) \quad (27)$$

$$\equiv V_{\text{dir}}(r) F_a(r) + [\hat{V}_{\text{ex}} F_a](r), \quad (28)$$

where now the  $b$  sum extends over all occupied *orbitals* (i.e.,  $b = \{n_b, \kappa_b\}$ ),  $y_{ab}^k$  is a symmetric Coulomb integral,

$$y_{ab}^k(r) = \int_0^\infty \frac{r_{<}^k}{r_{>}^{k+1}} [f_a f_b + g_a g_b](r') dr', \quad (29)$$

with  $r_{<} = \min(r, r')$ , and  $C_{ab}^k$  is the angular factor,

$$C_{ab}^k \equiv \langle \kappa_a || C^k || \kappa_b \rangle = (-1)^{j_a+1/2} \sqrt{[j_a][j_b]} \times \begin{pmatrix} j_a & j_b & k \\ -1/2 & 1/2 & 0 \end{pmatrix} \pi(l_a + l_b + k). \quad (30)$$

Here,  $\pi(x) = 1$  if  $x$  is even, but  $= 0$  if  $x$  is odd, and  $[x] = 2x+1$ . The  $x_b$  term is the occupation fraction for shell  $b$ , and  $\tilde{x}_b^a = x_b$

when  $b \neq a$ , but  $\tilde{x}_a^a = 1$  ( $x_b = 1$  for closed shell; this is an approximate way for treating HF equations for open-shell systems<sup>5</sup>). Note that the  $a = b$  term from  $V_{\text{ex}}$  can also be expressed as a local potential, and though it is stored in the  $V_{\text{ex}}$  matrix, can actually be thought of as part of the direct potential [it actually arises from the  $(n_i, \kappa_i) = (n_a, \kappa_a)$  term from the first integral on the RHS of Eq. (26)]. For example, when running for the ‘Hartree’ method (excluding exchange), it is kept.

### Hartree-Fock algorithm:

- Use a local approximation (guess) for  $V_{\text{el}}(r)$ <sup>6</sup> to form an initial set of core orbitals
- Begin HF routine:
  - Form new  $V_{\text{dir}}$ , Eq. (27)
  - For each orbital
    - \* Form new  $V_{\text{exch}}\phi$ , Eq. (27)
    - \* Guess new energy based on change in  $V$
    - \* Solve inhomogeneous Dirac Equation (Sec. 3.2)
    - \* Adjust energy until  $\phi$  is eigenstate (Sec. 3.3)
    - \* Damp orbitals (and/or potentials)
  - Define  $\epsilon_{\text{HF}} = |(\epsilon_{\text{new}} - \epsilon_{\text{old}})/\epsilon_{\text{new}}|$
  - Continue HF routine until  $\epsilon < \epsilon_{\text{cut}}$  for all states
- HF (core) has converged. “Freeze”  $V_{\text{dir}}$  and orbitals  $\{\phi_c\}$
- Do HF for each valence state (from “For each orbital”)

In the actual code, we perform the HF procedure for the core twice, first using an approximate localised form of the exchange potential  $V_{\text{exch}}$  (the first run is iterated until  $\epsilon$  reaches a reasonably small value, but doesn’t need to be continued until complete convergence). This extra step is not necessary, and is only done to speed up the convergence (so we have more realistic orbitals as a starting point for solving the non-local HF equations). The approximate potential will be shown in Sec. 3.4. Plots of the electron density ( $\rho = \sum_n |\psi_n|^2$ ) for Cs are shown in Fig. 3, as calculated in the Hartree-Fock and Hartree (no exchange) approximations, and using the local Green’s parametric potential [6], which is used as the HF starting potential.

The HF procedure converges to the level of  $\epsilon \simeq 10^{-13}$ . The resulting core orbitals are correct eigenstates (that is, the energy calculated in the HF routine is the same as  $\langle \phi | H | \phi \rangle$ ) to the level of  $\sim 10^{-10}$ ; see Table 3.1. The HF orbitals are also correctly orthogonal to better than  $\sim 10^{-6}$ ; e.g., for Cs, the orthogonality for the worst core-core and valence-valence states are calculated:  $\langle 5s_{1/2} | 4s_{1/2} \rangle = -1 \times 10^{-6}$  and  $\langle 7s_{1/2} | 6s_{1/2} \rangle = 3 \times 10^{-7}$ .

<sup>5</sup>The  $i$  sum in (26) includes a sum over all occupied  $m$  states; for partially filled shells, this doesn’t include all  $m$  values. So, to do the sum, we assume each  $m$  is filled with equal probability – i.e., that each  $m$  is partially filled. We assume non-relativistic filling (e.g.,  $p_{1/2}$  and  $p_{3/2}$  on equal footing).

<sup>6</sup>Essentially any approximation will do, so long as the combined nuclear and electronic potentials have  $V(r \rightarrow 0) \approx -Z/r$ , and  $V(r \rightarrow 0) \approx -\xi/r$ , where  $\xi = 1$  for a neutral atom. I use a simple two-parameter Green’s Potential [6].

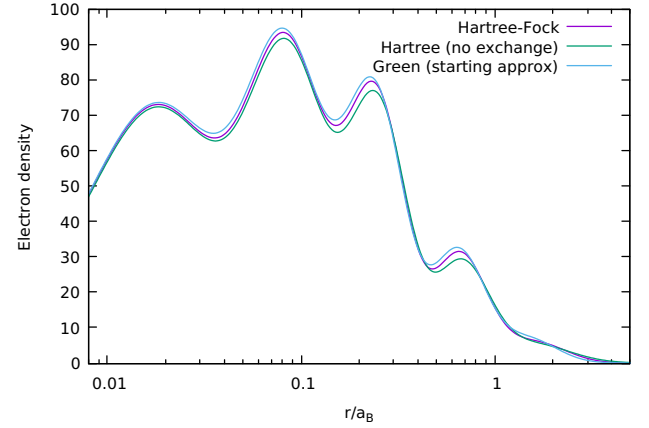


Figure 3: Electron density  $\rho = \sum_n |\psi_n|^2$  for Cs in the Hartree-Fock, Hartree, and local Green potential approximations.

### 3.2 Solving the HF equation for given orbital

To solve the HF equation for a given orbital, we use the Green’s method as outlined above. The HF Hamiltonian is split in to local and non-local parts as  $H_{\text{HF}} = H_l + V_{\text{nl}}$ , with

$$H_l = H_0 + V_{\text{nuc}} + fV_{\text{dir}}, \quad (31)$$

$$V_{\text{nl}} = (1 - f)V_{\text{dir}} + V_{\text{exch}}. \quad (32)$$

Here,

$$f = \begin{cases} (N_c - 1)/N_c & \text{core} \\ 1 & \text{valence} \end{cases} \quad (33)$$

is chosen so that  $V_l = V_{\text{nuc}} + fV_{\text{dir}} \rightarrow -Z_{\text{ion}}/r$  as  $r \rightarrow \infty$  (otherwise, we would have  $V_l \rightarrow 0$ ). This is done to ensure the existence of the homogenous solution that is regular at infinity ( $G_\infty$ ), and so that the asymptotic behaviour of the “ $G$ ” (homogenous) solutions (21) more closely match that of the final solution.

Then, the inhomogeneous equation to solve has the form of Eq. (20) as:

$$(H_l - \epsilon) F = -V_{\text{nl}} F. \quad (34)$$

Note that the “source” term in this case contains the solution  $F$ . So the equations must be solved iteratively, with some starting approximation for the source term, so that the solution at the  $n$ th step depends on the approximate solution from the previous step. Further,  $V_{\text{nl}}$  and  $H_l$  also depend on the solution  $F$  via (28), and these are also formed at the  $n$ th step using  $F^{(n-1)}$ . That is, the equation we solve at each step of the iterative procedure is

$$\begin{aligned} (H_0 + V_{\text{nuc}} + fV_{\text{dir}}^{(n-1)} - \epsilon) F^{(n)} = \\ - \left( (1 - f)V_{\text{dir}}^{(n-1)} + V_{\text{exch}}^{(n-1)} \right) F^{(n-1)}. \end{aligned} \quad (35)$$

The energy guess used for the  $(n+1)$ th step can be approximated as  $\epsilon^{(n)} + \delta\epsilon$ , with

$$\delta\epsilon \approx \frac{\langle F^{(n-1)} | \Delta V | F^{(n)} \rangle}{\langle F^{(n-1)} | F^{(n)} \rangle} \quad (36)$$

where  $\Delta V = V_{\text{HF}}^{(n)} - V_{\text{HF}}^{(n-1)}$ . Instead of storing  $F^{(n-1)}$ , we use  $F^{(0)}$  and calculate the energy guess with respect to  $\epsilon^{(0)}$ .



Table 1: Comparison of Hartree-Fock energies with expectation value of Hamiltonian for Cs (test of numerical accuracy).

$\psi$	$\langle\psi H \psi\rangle$	$\varepsilon_{\text{HF}}$	$\epsilon^*$	$\psi$	$\langle\psi H \psi\rangle$	$\varepsilon_{\text{HF}}$	$\epsilon$
1s	-1330.118815521	-1330.118815560	-3E-11	4d <sub>3/2</sub>	-3.48560407059	-3.48560407173	-3E-10
2s	-212.564435296	-212.564435324	-1E-10	4d <sub>5/2</sub>	-3.39688691127	-3.39688691211	-2E-10
2p <sub>1/2</sub>	-199.429442278	-199.429442294	-8E-11	5s	-1.48980152949	-1.48980153020	-5E-10
2p <sub>3/2</sub>	-186.436552433	-186.436552441	-5E-11	5p <sub>1/2</sub>	-0.90789515588	-0.90789515640	-6E-10
3s	-45.969703199	-45.969703209	-2E-10	5p <sub>3/2</sub>	-0.84033687303	-0.84033687355	-6E-10
3p <sub>1/2</sub>	-40.448262360	-40.448262367	-2E-10	Valence states:			
3p <sub>3/2</sub>	-37.894269602	-37.894269608	-2E-10	6s	-0.12736792294	-0.12736792298	-3E-10
3d <sub>3/2</sub>	-28.309463221	-28.309463222	-4E-11	7s	-0.05518731817	-0.05518731818	-2E-10
3d <sub>5/2</sub>	-27.775120363	-27.775120360	8E-11	6p <sub>1/2</sub>	-0.08561582043	-0.08561582050	-8E-10
4s	-9.512801927	-9.512801931	-4E-10	7p <sub>1/2</sub>	-0.04202136384	-0.04202136387	-6E-10
4p <sub>1/2</sub>	-7.446266669	-7.446266672	-4E-10	6p <sub>3/2</sub>	-0.08378541702	-0.08378541709	-8E-10
4p <sub>3/2</sub>	-6.920983364	-6.920983366	-4E-10	7p <sub>3/2</sub>	-0.04136802039	-0.04136802044	-1E-09

$$^*\epsilon \equiv (\langle\psi|H|\psi\rangle - \varepsilon_{\text{HF}})/\varepsilon_{\text{HF}}$$

In general, unless the initial energy guess was correct, these solutions will not be correct eigenstates of the HF Hamiltonian and therefore won't be correctly normalised. We therefore must make small adjustments to the energy and the orbital until  $F$  is properly normalised and thus an eigenstate of the Hamiltonian. This procedure is outlined in the next subsection 3.3.

Once the energy has been fine-tuned, and we have a normalised eigenstate, we continue the HF procedure. To aid convergence, however, we first “damp” the orbitals as:

$$F \rightarrow (1 - \eta)F + \eta F_{\text{old}}. \quad (37)$$

This both greatly increases the numerical stability, and speeds up the convergence (otherwise, orbitals tend to either oscillate between two values, or blow up). Typically,  $\eta \simeq 0.5$ ; in the code,  $\eta$  is initially set to a large value (0.8), and is slowly ramped down (to 0.1) over the HF iterations (0 means no damping). So long as the equations converge, the solutions do not depend on the value chosen.

(A slightly different method for including the non-local exchange part is given in Ref. [7] on pg. 462 [also [8] pg. 495].)

### 3.3 Energy adjustments – finding eigenstate

Assume the correct orbital and energy can be written as  $F + \delta F$ , and  $\varepsilon + \delta\varepsilon$ , where  $F$  was the solution to Eq. (35) using the trial energy  $\varepsilon$ . Subbing this back into the HF Dirac equation, we find a new inhomogenous equation (to first order):

$$(H_{\text{HF}} - \varepsilon)\delta F = \delta\varepsilon F \quad (38)$$

$$(H_1 - \varepsilon)\delta F = \delta\varepsilon F - V_{\text{nl}}\delta F, \quad (39)$$

which we solve iteratively for  $\delta F$  and  $\delta\varepsilon$ . As the first step, we divide (39) by the unknown  $\delta\varepsilon$ , set  $V_{\text{nl}}\delta F = 0$ , and solve for  $\tilde{F} \equiv \delta F/\delta\varepsilon$  using Green's method (22). Note that we don't need to re-solve the homogeneous equation (21), since we can re-use the  $G_\infty$ ,  $G_0$  solutions obtained when solving (35).

Since  $(F + \delta F)$  must be normalised, we find the first guess for  $\delta\varepsilon$  as (keeping only first-order terms):

$$\delta\varepsilon = \frac{\langle F|F \rangle - 1}{2\langle F|\tilde{F} \rangle}. \quad (40)$$

Then, using this  $\delta\varepsilon$  and  $\delta F = \delta\varepsilon\tilde{F}$ , we form  $V_{\text{nl}}\delta F$  and solve (39) for  $\delta F$ . Then, we make the corrections to the orbital and

energy:

$$F \rightarrow F + \delta F, \quad \varepsilon \rightarrow \varepsilon + \delta\varepsilon. \quad (41)$$

This iterative procedure is continued from Eq. (39) until the energy correction drops below a specified value (i.e., until  $F$  is properly normalised). The procedure converges very rapidly, and typically is converged (for  $\delta\varepsilon/\varepsilon$ ) to parts in  $10^{20}$  with just two iterations.

Note that, so long as it was chosen appropriately, the non-local term  $V_{\text{nl}}$  is small, and so the  $V_{\text{nl}}\delta F$  term is even smaller and can be excluded entirely in this section without having much of an impact. Including it, however, leads to better overall convergence of the HF equations. Note that  $V_{\text{nl}}\delta F$  includes  $V_{\text{exch}}\delta F$ , which must be calculated; to speed things up, we restrict this calculation to include only the  $k = 0$  terms [see Eq. (28)], which dominate by far.

### 3.4 Approximate “local” exchange potential

There are several methods for obtaining a localised approximation to the HF potential, a common example is the “Hartree-Fock-Slater” method [9]. Here, I outline a slightly different method; while decidedly more dodgy, it actually gives surprisingly good results. Note that we use this only as a starting point for the HF/TDHF procedures, so the the final result does not depend on this potential. The choice of a good starting approximation does, however, greatly speed up the convergence of the iterative procedures.

Introducing the notation  $v_{ab}^x$  [see Eq. (27)], the non-local exchange part of the HF potential can be expressed

$$[\hat{V}_{\text{ex}}F_a](r) = \sum_b v_{ab}^x(r)F_b(r). \quad (42)$$

It is non-local in that it cannot be expressed as  $\hat{V}_{\text{ex}}(r)F_a(r)$ . Multiply (42) from the right and divide by  $F_a^\dagger F_a$ :

$$\frac{[\hat{V}_{\text{ex}}F_a]F_a^\dagger}{F_a^\dagger F_a}F_a = \frac{\sum_b v_{ab}^x(r)F_b(r)F_a^\dagger(r)}{F_a^\dagger F_a}F_a(r) \quad (43)$$

$$\approx U_{\text{ex}}^{(a)}(r)F_a(r). \quad (44)$$

In this way we may define  $U_{\text{ex}}^{(a)}(r)$ , which is a localised exchange potential (for state  $a$ ). Note that  $U(r)$  is different for each state, and depends on the  $F_a$  orbital, and therefore must itself be found iteratively.

In theory, this is exact except for when  $F_a^\dagger F_a = 0$ . In practice, it is very numerically unstable whenever  $F_a^\dagger F_a$  is small. However, this is not a major problem, since when  $F_a$  is small, we don't care what the exchange potential is. We proceed by introducing a cut-off,  $\lambda_a$ , and only calculating the exchange potential when  $F_a$  is not small. Therefore, we write

$$U_{\text{ex}}^{(a)}(r) = v_{aa}^x(r) + \sum_{b \neq a} v_{ab}^x(r) \Lambda(r) \quad (45)$$

with

$$\Lambda(r) = \begin{cases} \frac{F_a^\dagger(r) F_b(r)}{F_a^\dagger F_a} & |F_a(r)| > \lambda_a \\ 0 & \text{otherwise} \end{cases} \quad (46)$$

Of course, we don't apply the cut-off when  $b = a$  in the sum, since here the cancellation is exact and there is no numerical instability. In fact, this  $a = b$  term actually gives the dominating contribution to the exchange potential. Partly, the reason this method gives such good results already is that the dominating case is treated exactly.

In the code, the cut-off is taken as

$$\lambda_a = 10^{-2} |f_a|^{\text{max}},$$

where  $|f|^{\text{max}}$  is the maximum magnitude for the upper  $f(r)$  component of  $F_a$ . Making the cut-off too small introduces numerical instabilities.

This potential leads to very good approximations for the HF orbitals and energies, and as such leads to very quick convergence of both HF and TDHF equations. For example, with normal grid choices, the energies agree with complete HF energies to five digits, and the core orbitals are orthogonal to the level of  $10^{-4} - 10^{-5}$ .

## 4 External fields

### 4.1 Time-dependent Hartree-Fock

In the presence of a time-varying external field with frequency  $\omega$ , the orbitals will contain time-varying perturbations:

$$\psi \rightarrow \psi + \delta\psi_- e^{-i\omega t} + \delta\psi_+ e^{i\omega t}, \quad (47)$$

with  $\varepsilon \rightarrow \varepsilon + \delta\varepsilon$ . Keeping terms only to first-order, the corrections are seen to satisfy the equation (e.g., [10]):

$$\begin{aligned} (H_{\text{HF}} - \varepsilon - \omega) \delta\psi_- &= -(\hat{h} + \delta V - \delta\varepsilon) \psi \\ (H_l - \varepsilon - \omega) \delta\psi_- &= -V_{nl} \delta\psi - (\hat{h} + \delta V - \delta\varepsilon) \psi \end{aligned} \quad (48)$$

(similarly for  $\psi_+$ , but with  $\hat{h} \rightarrow \hat{h}^\dagger$  and  $\delta V \rightarrow \delta V^\dagger$ ), where  $\hat{h}$  is the operator for the external field. Here,  $\delta V$  is the correction to the HF potential arising due to the correction  $\delta\psi_c$  to each of the core orbitals. This is a very important correction that will be discussed in the next section; for now, however, we will drop this term and just focus on solving these inhomogenous equations.

Note that, in general, the correction  $\delta\psi$  is not a state of definite  $j$ . We expand  $\delta\psi$  in terms of states  $\delta\psi_\kappa$  of definite  $\kappa$  (partial waves of definite angular momentum and parity):

$$\delta\psi = \sum_{\kappa} \delta\psi_{\kappa}. \quad (49)$$

For a scalar operator, there is only a single term in the sum  $|\kappa| = |\kappa|$  (i.e.,  $\Delta j = 0$ ), with parity determined by  $\kappa$  and the parity of the operator (here  $\kappa$  is for unperturbed state  $\psi_\kappa$ ,  $\kappa$  is for correction  $\delta\psi_\kappa$ ). For a vector operator,  $\Delta j = \pm 1, 0$  and so on. Note that  $\{\delta\psi_\kappa\}$  are orthogonal (and also are orthogonal to  $\psi$ ), and form a linearly independent set of solutions to (48).

To find the solutions to (48), express the Hamiltonian as

$$H_l = H_0 + V_{\text{nuc}} + V_{\text{dir}} + U_x \quad (50)$$

$$V_{nl} = V_{\text{exch}} - U_x, \quad (51)$$

where  $U_x$  is a local approximation to the exchange potential. In the simplest case, it is  $(f-1)V_{\text{dir}}$ , but better approximations aid the convergence (we use that from Sec. 3.4). It is desirable to make the effect of  $V_{nl}$  as small as possible.

For a single  $\kappa$ , we solve the equation iteratively as

$$\begin{aligned} (H_l - \varepsilon \pm \omega) \delta\psi_{\kappa}^{(n)} &= \\ &= (V_{nl} \delta\psi_{\kappa})^{(n-1)} - (\hat{h} - \delta\varepsilon^{(n-1)} \delta_{\kappa\kappa}) \psi_{\kappa} \end{aligned} \quad (52)$$

with  $V_{nl} \delta\psi_{\kappa} = 0$  initially. The solution is

$$\delta\psi_{\kappa} = \frac{\phi_{\kappa}^{\infty}}{c\omega} \int_0^r \{\phi_{\kappa}^0 | S\} r^2 dr' + \frac{\phi_{\kappa}^0}{c\omega} \int_r^{\infty} \{\phi_{\kappa}^{\infty} | S\} r^2 dr' \quad (53)$$

The  $\phi_{\kappa}^{0,\infty}$  functions here are the solutions with Dirac quantum number  $\kappa$  to the inhomogenous equation (21), including both the angular part and the  $1/r$ , and the “partial” matrix element includes only the integral over angular coordinates:

$$\{\psi_a | \hat{h} | \psi_b\} \equiv \int \psi_a^\dagger \hat{h} \psi_b d\Omega.$$

We similarly define the “partial” reduced matrix element via:

$$\{\psi_a | T_q^k | \psi_b\} \equiv (-1)^{j_a - m_a} \begin{pmatrix} j_a & k & j_b \\ -m_a & q & m_b \end{pmatrix} \{\psi_a || T^k || \psi_b\} \quad (54)$$

$$\equiv \Upsilon_{ab}^k \{\psi_a || T^k || \psi_b\}, \quad (55)$$

where the second line just introduced the shorthand  $\Upsilon_{ab}$ .

We divide Eq. (53) by  $\Upsilon$ , and solve the DE in terms of the projection

$$\widetilde{\delta\psi}_{\kappa} = \frac{1}{\Upsilon_{\kappa,\kappa}} \delta\psi_{\kappa}. \quad (56)$$

This is done so that one needs only to calculate the ( $m$ -independent) reduced matrix element of the  $\hat{h}$  operator when solving for  $\delta\psi$ . The radial integral  $|\delta\psi|^2$  is used to control convergence here (for including the non-local exchange part). Using  $U_x$  from Sec. 3.4, convergence (for a given orbital) to parts in  $10^9$  is typically reached in 10-20 iterations with no damping.

Note that from perturbation theory, the correction (excluding  $\delta V$  and considering case with  $\delta\varepsilon = 0$ ) can also be expressed as:

$$|\delta\psi_-\rangle = \sum_n \frac{|n\rangle \langle n | \hat{h} | \psi \rangle}{\varepsilon - \varepsilon_n + \omega}, \quad (57)$$

which can be used to test the method. Consider, e.g., the matrix element:

$$\langle m | \delta\psi \rangle = \frac{\langle m | \hat{h} | \psi \rangle}{\varepsilon - \varepsilon_m + \omega}, \quad (58)$$

$$\langle m | \widetilde{\delta\psi} \rangle = \frac{\langle m | \hat{h} | \psi \rangle}{\varepsilon - \varepsilon_m + \omega}, \quad (59)$$

Table 2: Testing TDHF method using Eq. (59) for Cs, with  $m = 6p_{1/2}$ ,  $\psi = 6s_{1/2}$  (Hartree-Fock level, no  $\delta V$ ).

Operator	(59) lhs	(59) rhs	$\epsilon^*$
$h_{E1} \quad (\omega = \omega_{HF})$	63.2029312	63.2025676	$6 \times 10^{-6}$
$h_{E1} \quad (\omega = 0)$	126.405501	126.405135	$3 \times 10^{-6}$
$h_{PNC} \quad (\omega = 0)$	-1.0700928	-1.0700932	$4 \times 10^{-7}$

$$^* \epsilon \equiv (lhs - rhs)/lhs$$

which can be calculated both ways (lhs vs rhs); see Table 2.

An important application of this technique is that it allows calculations to be done without requiring a summation over the complete set of intermediate states (replaced by solving the inhomogeneous differential equation). This method of performing exact summation over intermediate states is sometimes called the Solving Equations method, the Mixed States method, or the Dalgarno-Lewis method [11], depending on context. Note that in this example (59) the intermediate-states summation is trivial, since it involves only single operator and hence only a single intermediate state contributes. In general, all intermediate states (including continuum and positive energy states) contribute, so this method allows calculations with the need for a large basis.

## 4.2 Core polarisation (RPA)

[This is not yet fully implemented in the code]

This section largely follows Ref. [10] (see also [12–14]). In the presence of an external field, the core electrons become perturbed, and thus a correction to the frozen-core HF potential is induced. This effect is often called the core polarisation. The method described here is equivalent to and is often referred to as the random phase approximation (RPA).

Here, we use the notation:

$$\psi \rightarrow \psi + \delta\psi = \psi + \chi e^{-i\omega t} + \eta e^{i\omega t}. \quad (60)$$

To account for core polarisation, the set of TDHF equations:

$$\begin{aligned} (H_{HF} - \varepsilon - \omega) \chi_c &= -(\hat{h} + \delta V - \delta\varepsilon) \psi_c \\ (H_{HF} - \varepsilon + \omega) \eta_c &= -(\hat{h}^\dagger + \delta V^\dagger - \delta\varepsilon) \psi_c \end{aligned} \quad (61)$$

are solved self-consistently for the core. The two equations (61) are solved for each core orbital by expanding  $\chi_c$  over partial waves (49) and using the method from Sec. 4.1. Note that after integrating over angles the  $\delta\varepsilon$  term only appears in the equations when  $\varkappa = \kappa_c$  – which for odd-parity operators is never the case.

The  $\delta V$  term is the correction to the HF potential due to the action of the external field on the core electrons:

$$\delta V = V_{HF}(\{\psi_c + \delta\psi_c\}) - V_{HF}(\{\psi_c\}), \quad (62)$$

where  $\{\psi_c\}$  denotes the set of all core orbitals. This is typically a very important correction since it involves corrections to the HF potential that include a single core excitation (in the absence of external fields, there are no corrections to the HF potential involving only a single excitation). And the single-particle energy correction is

$$\delta\varepsilon_c = \langle \psi_c | \hat{h} + \delta V | \psi_c \rangle. \quad (63)$$

The  $\delta V$  and  $\delta\varepsilon$  terms are updated at each step of the iteration, and equations (61) are re-solved until convergence is reached ( $\delta V = 0$  for the initial iteration).

If  $\hat{h}$  is an operator of rank  $k$ , and using notation such that the  $\chi$  correction to the  $\psi_b$  orbital is written as:  $\chi_{(b)} = \sum_\beta \chi_\beta$  [see (49)], the reduced matrix elements of  $\delta V$  are:

$$\begin{aligned} \langle \chi_\alpha | \delta V | \psi_a \rangle &= \frac{(-1)^{k+1}}{[k]} \sum_{b\beta} \left( (-1)^{j_\alpha + j_\beta} (Q_{\alpha b a \beta}^k + Q_{\alpha b a \tilde{\beta}}^k) \right. \\ &\quad [k] \sum_\lambda \left[ (-1)^{j_\beta + j_b} \begin{Bmatrix} j_a & j_\alpha & k \\ j_b & j_\beta & \lambda \end{Bmatrix} Q_{\alpha a b \tilde{\beta}} \right. \\ &\quad \left. \left. + (-1)^{j_\alpha + j_b} \begin{Bmatrix} j_a & j_\alpha & k \\ j_\beta & j_b & \lambda \end{Bmatrix} Q_{\alpha b \beta a} \right] \right), \end{aligned} \quad (64)$$

where the sum  $b$  runs over all core orbitals, and  $\beta$  runs over all (partial wave) corrections to  $b$ . Here, the tilde ( $\tilde{\beta}$ ) means the  $\eta_\beta$  orbital is used; no tilde means  $\chi_\beta$ . The equation for  $\langle \eta_\alpha | \delta V^\dagger | \psi_a \rangle$  is the same, but with  $\chi_\alpha \rightarrow \eta_\alpha$  and  $\chi_\beta \leftrightarrow \eta_\beta$ . (This formula was taken from Ref. [12], and has not been checked.)

Here, the Coulomb integral  $Q$  is defined as

$$Q_{abcd}^k = (-1)^k \tilde{C}_{ac}^k \tilde{C}_{bd}^k R_{abcd}^k, \quad (65)$$

where

$$\tilde{C}_{ab}^k \equiv (-1)^{j_a + 1/2} C_{ab}^k \equiv (-1)^{j_a + 1/2} \langle \kappa_a | C^k | \kappa_b \rangle, \quad (66)$$

$C_{ab}^k$  is given by Eq. (30),

$$R_{abcd}^k \equiv \int dr_1 [f_a(r_1) f_c(r_1) + g_a(r_1) g_c(r_1)] y_{bd}^k(r_1), \quad (67)$$

and  $y_{bd}^k$  is given by Eq. (29). The  $Q_{abcd}^k$  integral is convenient due to the symmetries  $c \leftrightarrow a$ ,  $b \leftrightarrow d$ ,  $(ac) \leftrightarrow (bd)$ : ( $Q_{abcd}^k = Q_{cbad}^k = Q_{adcb}^k = Q_{cdab}^k = Q_{badc}^k = Q_{bcda}^k = Q_{dabc}^k = Q_{dcba}^k$ ); the same symmetries exist for  $R$ .

In this method, matrix elements of the operator  $\hat{h}$  between valence states  $v$  and  $w$  are calculated, including the effect of core polarisation (i.e., including the effect of  $\hat{h}$  operating on the core electrons) as [10]

$$\langle w | \hat{h} + \delta V | v \rangle, \quad (68)$$

which is equivalent to the RPA method (see, e.g., Ref. [2]). If the equations (61) are solved just once, without further iterations, this corresponds to the lowest (first) order corrections to the amplitude, which are shown diagrammatically in Fig. 4. Further iterations correspond to higher-orders. Once the equations have converged, the core polarisation is taken into account to all-orders.

The core polarisation can be included into mixed states (Dalgarno-Lewis) method for exact summation over intermediate states by solving the equations similar to (61), but for the required valence states (including the  $\delta V$ ).

Including the core-polarisation, the equation for the corrections becomes:

$$\frac{\delta\psi_\varkappa}{\Upsilon_{\varkappa,\kappa}} = \frac{\phi_\varkappa^\infty}{cw} \int_0^r \{ \phi_\varkappa^\infty | S \} r^2 dr' + \frac{\phi_\varkappa^0}{cw} \int_r^\infty \{ \phi_\varkappa^\infty | S \} r^2 dr' \quad (69)$$

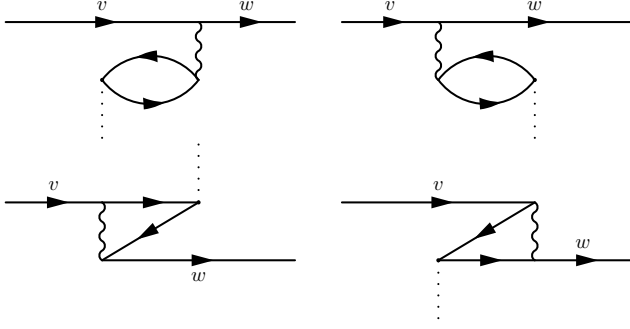


Figure 4: Diagrams representing the lowest order direct and exchange core-polarisation (RPA) corrections to the  $\langle w|\hat{h}|v\rangle$  amplitude. Wavy line is Coulomb interaction, dotted line is external field ( $\hat{h}$ ). All internal lines are summed over: forwards lines are virtual excited states, backward lines are holes in the core. In higher-order diagrams, each  $\hat{h}$  vertex is corrected again (RPA).

where

$$\{\phi_{\mathcal{K}}|S\} = -\left\{\phi_{\mathcal{K}}|\hat{h}|\psi_{\kappa}\right\} - \left\{\phi_{\mathcal{K}}|V_{\text{nl}}|\widetilde{\delta\psi_{\mathcal{K}}}\right\} - \left\{\phi_{\mathcal{K}}|\delta V|\psi_{\kappa}\right\} + \delta\varepsilon\delta_{\mathcal{K}\kappa}\{\phi_{\mathcal{K}}|\psi_{\kappa}\} \quad (70)$$

[note that the second term is just a radial integral, see, e.g., Eq. (27)].

## Appendix

Some useful equations, definitions are given; see, e.g., [2, 13, 15–18]. Note that I have introduced some notation not found in the above sources, and some of the notation differs between sources.

### A Coulomb Integrals

The Coulomb integral  $g_{abcd}$  can be expressed:

$$g_{abcd} \equiv \int d\mathbf{r}_1 d\mathbf{r}_2 \psi_a^\dagger(\mathbf{r}_1) \psi_b^\dagger(\mathbf{r}_2) \frac{1}{|\mathbf{r}_{12}|} \psi_c(\mathbf{r}_1) \psi_d(\mathbf{r}_2) \quad (71)$$

$$= \sum_{kq} (-1)^q \langle \kappa_a m_a | C_{-q}^k | \kappa_c m_c \rangle \langle \kappa_b m_b | C_q^k | \kappa_d m_d \rangle R_{abcd}^k,$$

where we used the Laplace expansion:

$$\frac{1}{r_{12}} = \sum_{kq} \frac{r_{<}^k}{r_{>}^{k+1}} (-1)^q C_{-q}^k(\mathbf{n}_1) C_q^k(\mathbf{n}_2), \quad (72)$$

with  $r_{<} = \min(r, r')$ , and

$$C_q^k \equiv \sqrt{\frac{4\pi}{2k+1}} Y_{kq}(\mathbf{n}). \quad (73)$$

The  $R_{abcd}^k$  factor is defined as:

$$R_{abcd}^k = \int d\mathbf{r}_1 [f_a(r_1) f_c(r_1) + g_a(r_1) g_c(r_1)] y_{bd}^k(r_1) \quad (74)$$

which has symmetry:  $c \leftrightarrow a$ ,  $b \leftrightarrow d$ ,  $(ac) \leftrightarrow (bd)$ :

$$R_{abcd}^k = R_{cbad}^k = R_{adcb}^k = R_{cdab}^k = R_{badc}^k = R_{bdcda}^k = R_{dabc}^k = R_{dcba}^k, \quad (75)$$

and the symmetric  $y_{bd}^k(r) = y_{db}^k(r)$  integral is defined:

$$y_{bd}^k(r) = \int_0^\infty \frac{r_{<}^k}{r_{>}^{k+1}} [f_a f_b + g_a g_b](r') dr'. \quad (76)$$

Note that:

$$\langle \kappa_a || C^k || \kappa_b \rangle \equiv C_{ab}^k \equiv (-1)^{j_a+1/2} \tilde{C}_{ab}^k, \quad (77)$$

$$= (-1)^{j_a+1/2} \sqrt{[j_a][j_b]} \begin{pmatrix} j_a & j_b & k \\ -1/2 & 1/2 & 0 \end{pmatrix} \pi(l_a, l_b, k) \quad (78)$$

where  $\tilde{C}_{ac}^k$  is a short-hand notation that is useful since  $\tilde{C}_{ac}^k = \tilde{C}_{ca}^k$ .

$$\sum_{m_b} g_{abab} = [j_b] R_{abab}^0. \quad (79)$$

We further define the useful integrals:

$$X_{abcd}^k \equiv (-1)^k \langle \kappa_a || C^k || \kappa_c \rangle \langle \kappa_b || C^k || \kappa_d \rangle R_{abcd}^k \quad (80)$$

$$= (-1)^{j_a+j_b+1} Q_{abcd}^k,$$

$$Q_{abcd}^k = (-1)^k \tilde{C}_{ac}^k \tilde{C}_{bd}^k R_{abcd}^k \quad (81)$$

and

$$Z_{abcd}^k \equiv X_{abcd}^k + \sum_{\lambda} [k] \begin{Bmatrix} j_c & j_a & k \\ j_d & j_b & \lambda \end{Bmatrix} X_{abdc}^{\lambda} \quad (82)$$

$$= (-1)^{j_a+j_b+1} \left( Q_{abcd}^k + \sum_{\lambda} [k] \begin{Bmatrix} j_c & j_a & k \\ j_d & j_b & \lambda \end{Bmatrix} Q_{abdc}^{\lambda} \right).$$

Here  $Q_{abcd}^k$  is convenient due to the symmetries  $c \leftrightarrow a$ ,  $b \leftrightarrow d$ ,  $(ac) \leftrightarrow (bd)$ :

$$Q_{abcd}^k = Q_{cbad}^k = Q_{adcb}^k = Q_{cdab}^k = Q_{badc}^k = Q_{bdcda}^k = Q_{dabc}^k = Q_{dcba}^k. \quad (83)$$

### B Angular integrals + identities

#### Wigner-Eckhardt theorem

See, e.g., Refs. [16, 17]:

$$\langle n_a \kappa_a m_a | T_q^k | n_b \kappa_b m_b \rangle = (-1)^{j_a-m_a} \begin{pmatrix} j_a & k & j_b \\ -m_a & q & m_b \end{pmatrix} \langle n_a \kappa_a || T^k || n_b \kappa_b \rangle \quad (84)$$

$$\langle j || T^k || j' \rangle = (-1)^{j-j'} \langle j' || T^k || j \rangle^* \quad (85)$$

$$\langle J' I F' || T^k || J I F \rangle = (-1)^{F+J'+I+k} \sqrt{[F'] [F]} \begin{Bmatrix} J & I & F \\ F' & k & J' \end{Bmatrix} \langle J' || T^k || J \rangle \quad (86)$$

where  $([a] \equiv 2a+1)$ .

$$\sum_{m_a, m_b, q} |\langle n_a \kappa_a m_a | T_q^k | n_b \kappa_b m_b \rangle|^2 = |\langle n_a \kappa_a || T^k || n_b \kappa_b \rangle|^2. \quad (87)$$

#### Clebsch-Gordon coefficients notation

$$\langle j_1 m_1, j_2 m_2 | J M \rangle \equiv (-1)^{j_1-j_2+M} \sqrt{[J]} \begin{pmatrix} j_1 & j_2 & J \\ m_1 & m_2 & -M \end{pmatrix} \quad (88)$$

$$\equiv C(j_1, j_2, J; m_1, m_2, M) \quad (89)$$

$$\equiv C_{j_1 m_1, j_2 m_2}^{J M}. \quad (90)$$

$$|j_1 j_2; J M\rangle = \sum_{m_1, m_2} \langle j_1 m_1, j_2 m_2 | J M \rangle |j_1 m_1\rangle |j_2 m_2\rangle \quad (91)$$



## Some angular integrals + matrix elements

$$\int Y_{l'm'} Y_{lm} Y_{LM} d\Omega = \sqrt{\frac{[l'] [l] [L]}{4\pi}} \begin{pmatrix} l' & l & L \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l' & l & L \\ m' & m & M \end{pmatrix} \quad (92)$$

$$\sum_{jm} (2j+1) \begin{pmatrix} j_1 & j_2 & j \\ m_1 & m_2 & m \end{pmatrix} \begin{pmatrix} j_1 & j_2 & j \\ m'_1 & m'_2 & m \end{pmatrix} = \delta_{m_1 m'_1} \delta_{m_2 m'_2} \quad (93)$$

$$\sum_{m_1 m_2} (2j+1) \begin{pmatrix} j_1 & j_2 & j \\ m_1 & m_2 & m \end{pmatrix} \begin{pmatrix} j_1 & j_2 & j' \\ m_1 & m_2 & m' \end{pmatrix} = \delta_{jj'} \delta_{mm'} \quad (94)$$

$$\sum_{m_l=-l}^l |Y_{lm_l}|^2 = \frac{2l+1}{4\pi} \quad (95)$$

$$\sum_m |\Omega_{\kappa m}|^2 = \frac{2j+1}{4\pi} \quad (96)$$

$$\langle \kappa_a || C^k || \kappa_b \rangle = (-1)^{j_a+1/2} \sqrt{[j_a][j_b]} \begin{pmatrix} j_a & j_b & k \\ -1/2 & 1/2 & 0 \end{pmatrix} \pi(l_a + l_b + k) \quad (97)$$

$\pi(x) = 1$  if  $x$  is even, but  $= 0$  if  $x$  is odd.

$$\langle l_a || C^k || l_b \rangle = (-1)^{l_a} \sqrt{[l_a][l_b]} \begin{pmatrix} l_a & l_b & k \\ 0 & 0 & 0 \end{pmatrix} \quad (98)$$

$$\langle n\kappa || r_z || n'\kappa' \rangle = (n\kappa | r | n'\kappa') \langle \kappa || C^1 || \kappa' \rangle \quad (99)$$

From Ch. 13 of Ref. [17]:

$$\langle jls || l || j'l's' \rangle = \delta_{ll'} \delta_{ss'} (-1)^{j'+l+s+1} \sqrt{[j][j'][l]l(l+1)} \begin{Bmatrix} j & 1 & j' \\ l & s & l \end{Bmatrix} \quad (100)$$

$$\langle jls || s || j'l's' \rangle = \delta_{ll'} \delta_{ss'} (-1)^{j+l+s+1} \sqrt{[j][j'][s]s(s+1)} \begin{Bmatrix} j & 1 & j' \\ s & l & s \end{Bmatrix} \quad (101)$$

## C Useful definitions/identities

### Dirac matrices

Dirac matrices are defined by the relation:

$$\{\gamma^\mu, \gamma^\nu\} = 2g^{\mu\nu}, \quad (102)$$

and have the properties:

$$\gamma^i \gamma^0 = -\gamma^0 \gamma^i. \quad (103)$$

In the Dirac basis, they have the form:

$$\gamma^0 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad \gamma^a = \begin{pmatrix} 0 & \sigma^a \\ -\sigma^a & 0 \end{pmatrix}, \quad \gamma^5 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}. \quad (104)$$

It is often convenient to also define:  $\gamma^5 \equiv i\gamma^0\gamma^1\gamma^2\gamma^3$ .

### Pauli spin matrices:

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad (105)$$

$$\sigma_i \sigma_j = i\epsilon_{ijk} \sigma_k + \delta_{ij}, \quad [\sigma_i, \sigma_j] = 2i\epsilon_{ijk} \sigma_k \quad (106)$$

$$(\sigma \cdot a)(\sigma \cdot b) = a \cdot b + i\sigma \cdot (a \times b) \quad (107)$$

## Dirac equation (in Dirac basis)

Orbitals are written (for spherical potential):

$$\phi_{n\kappa m}(\mathbf{r}) = \begin{pmatrix} f_{n\kappa}(r) \Omega_{\kappa m}(\mathbf{n}) \\ ig_{n\kappa}(r) \Omega_{-\kappa, m}(\mathbf{n}) \end{pmatrix}, \quad (108)$$

$$\Omega_{\kappa m}(\mathbf{n}) = \sum_{\sigma=\pm 1/2} \langle l, m-\sigma, 1/2, \sigma | j, m \rangle Y_{l, m-\sigma}(\mathbf{n}) \chi_\sigma \quad (109)$$

$$= \begin{pmatrix} (-1)^{j-l-1/2} \sqrt{\frac{\kappa+1/2-m}{2\kappa+1}} Y_{l, m-1/2}(\theta, \phi) \\ \sqrt{\frac{\kappa+1/2+m}{2\kappa+1}} Y_{l, m+1/2}(\theta, \phi) \end{pmatrix} \quad (110)$$

(with  $l \equiv |\kappa + 1/2| - 1/2$ ), where

$$\kappa = (l-j)(2j+1), \quad l = |\kappa + 1/2| - 1/2, \quad j = |\kappa| - 1/2. \quad (111)$$

The DE can also be written in radial form as

$$\begin{pmatrix} V - \varepsilon & c(-\partial_r + \frac{\kappa}{r}) \\ c(\partial_r + \frac{\kappa}{r}) & V - \varepsilon - 2c^2 \end{pmatrix} \begin{pmatrix} f_{n\kappa} \\ g_{n\kappa} \end{pmatrix} = 0. \quad (112)$$

Some useful identities:

$$(\sigma \cdot \mathbf{p}) y(r) \Omega_{\kappa m} = i \left( y' + \frac{\kappa+1}{r} y \right) \Omega_{-\kappa, m} \quad (113)$$

$$(\sigma \cdot \mathbf{n}) \Omega_{\kappa m} = -\Omega_{-\kappa, m}, \quad (114)$$

and

$$[\mathbf{p}, y] \phi = \phi(\mathbf{p}y). \quad (115)$$

## References

- [1] H. A. Bethe and E. E. Salpeter, *Quantum mechanics of one- and two-electron atoms* (Plenum Publishing Corporation, New York, 1977).
- [2] W. R. Johnson, *Atomic Structure Theory* (Springer, New York, 2007).
- [3] V. A. Dzuba, O. P. Sushkov, and V. V. Flambaum, *Prepr. INP 82-89 INP 82-89* (1982).
- [4] I. Lindgren and J. Morrison, *Atomic many-body theory*, 2nd ed. (Springer-Verlag, New York, 1986).
- [5] G. B. Arfken, H. J. Weber, and F. E. Harris, *Mathematical Methods for Physicists* (Elsevier, 2013).
- [6] A. E. S. Green, D. L. Sellin, and A. S. Zachor, *Phys. Rev.* **184**, 1 (1969).
- [7] V. A. Dzuba, V. V. Flambaum, P. G. Silvestrov, and O. P. Sushkov, *Phys. Lett. A* **131**, 461 (1988).
- [8] V. A. Dzuba, V. V. Flambaum, and O. P. Sushkov, *Phys. Lett. A* **140**, 493 (1989).
- [9] J. C. Slater, *Phys. Rev.* **81**, 385 (1951).
- [10] V. A. Dzuba, V. V. Flambaum, and O. P. Sushkov, *J. Phys. B* **17**, 1953 (1984).
- [11] A. Dalgarno and J. T. Lewis, *Proceedings of the Royal Society A* **233**, 70 (1955).
- [12] V. A. Dzuba, J. C. Berengut, J. S. M. Ginges, and V. V. Flambaum, *Phys. Rev. A* **98**, 043411 (2018), arXiv:1805.04989.
- [13] N. L. Manakov, V. D. Ovsiannikov, and L. P. Rapoport, *Phys. Rep.* **141**, 320 (1986).
- [14] W. R. Johnson, C. D. Lin, K. T. Cheng, and C. M. Lee, *Phys. Scr.* **21**, 409 (1980).
- [15] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics: Non-relativistic Theory* (Pergamon, Oxford, 1977).
- [16] I. I. Sobelman, *Atomic Spectra and Radiative Transitions* (Springer, Berlin, Heidelberg, 1992).
- [17] D. A. Varshalovich, A. N. Moskalev, and V. K. Khersonskii, *Quantum Theory of Angular Momentum* (World Scientific, Singapore, 1988).
- [18] J. J. Sakurai, *Modern Quantum Mechanics* (2011).