

221B Lecture Notes

Many-Body Problems II

Atomic Physics

1 Single-Electron atoms

When there is only one electron going around a nucleus, it is a hydrogen-like atom: H, He⁺, Li⁺⁺, Be³⁺, etc. The energy levels of the electron is well-known, determined only by the principal quantum number n

$$E_n = -\frac{1}{2} \frac{Z^2 e^2}{a_B}, \quad (1)$$

where $a = \hbar^2/m_e e^2$ is the Bohr radius. Some of the wave functions which we will use later on are

$$\psi_{1s}(\vec{x}) = a^{-3/2} 2e^{-r/a} Y_0^0(\theta, \phi) \quad (2)$$

$$\psi_{2s}(\vec{x}) = a^{-3/2} \frac{1}{\sqrt{2}} \left(1 - \frac{r}{2a}\right) e^{-r/2a} Y_0^0(\theta, \phi) \quad (3)$$

$$\psi_{2p}(\vec{x}) = a^{-3/2} \frac{\sqrt{6}}{12} \frac{r}{a} e^{-r/2a} Y_1^m(\theta, \phi). \quad (4)$$

Here, $a = a_B/Z$.

As we discussed in 221A, the fine splittings arise due to the relativistic effects, namely the relativistic correction

$$H_{rc} = -\frac{(\vec{p}^2)^2}{8m^3 c^2}, \quad (5)$$

the spin-orbit coupling

$$H_{LS} = +g \frac{1}{4m_e^2 c^2} \frac{1}{r} \frac{dV_c}{dr} (\vec{L} \cdot \vec{S}), \quad (6)$$

and the Darwin term

$$H_{\text{Darwin}} = \frac{\hbar^2}{8m_e^2 c^2} \Delta V_c. \quad (7)$$

The energy levels are given by nl_j , where $j = l \pm \frac{1}{2}$. There remains an accidental degeneracy among states with the same n and j , such as $2s_{1/2}$ and

$2p_{1/2}$, $3p_{3/2}$ and $3d_{3/2}$, etc. This degeneracy will be removed by the Lamb shift, which will be discussed towards the end of the course.

In addition, there is the hyperfine interaction between the electron and the nucleus which we will not discuss in this notes.

2 Two-Electron atoms

Multi-electron atoms are quite complicated. In addition to the central potential due to the nuclear charge, there are repulsive Coulomb potentials among electrons. The Hamiltonian is

$$H = \sum_i \left(\frac{\vec{p}_i^2}{2m} - \frac{Ze^2}{r_i} \right) + \sum_{i < j} \frac{e^2}{r_{ij}}. \quad (8)$$

Here, $r_i = |\vec{x}_i|$ and $r_{ij} = |\vec{x}_i - \vec{x}_j|$. Because of the Coulomb interaction among electrons, one cannot solve the system exactly anymore (at least analytically). Various techniques are devised to attack this problem, which we will discuss below. For concreteness, let us consider Helium atom, or in general a nucleus of charge Ze and two electrons.

2.1 Perturbation Theory

The simplest approach (at least conceptually) is to apply perturbation theory to study the atomic structure, starting from one-particle wave functions and their Slater determinants.

It is obvious from the beginning that the use of perturbation theory is conceptually flawed. We treat the Coulomb attraction between each electron and the nucleus exactly, while treating the Coulomb repulsion between two electrons as a perturbation to the system. It is formally justified, if Z is very large with only two electrons; then the Coulomb attraction is enhanced by Z , while the Coulomb repulsion is not. The perturbative treatment of the Coulomb repulsion can be viewed as an expansion in $1/Z$. In fact, we will see that the perturbation theory gives good results for positive ions with only two electrons, while it does not work very well for H^- . We will then improve it by a variation method, which improves the agreement between the calculation and the data.

| | $-E_{\text{exp}}(\text{eV})$ | $-E_0$ | $-E_0 + E_{ee}$ | $-E_{\text{var}}$ |
|------------------|------------------------------|--------|-----------------|-------------------|
| H ⁻ | 14.36 | 27.06 | 10.15 | 12.79 |
| He | 78.62 | 108.24 | 74.42 | 77.06 |
| Li ⁺ | 197.14 | 243.54 | 192.80 | 195.45 |
| Be ⁺⁺ | 369.96 | 432.96 | 365.31 | 367.95 |
| B ³⁺ | 596.4 | 676.50 | 591.94 | 594.58 |
| C ⁴⁺ | 876.2 | 974.16 | 872.69 | 875.33 |

Table 1: Binding energies as measured E_{exp} , E_0 calculated with the single-particle Hamiltonian H_0 , with electron Coulomb self-energy added at the 1st order in perturbation $E_0 + E_{ee}$, and improvement with the variational method E_{var} for two-electron atoms. The numbers are from “Introduction to Quantum Mechanics,” Linus Pauling and E. Bright Wilson, Jr., McGraw-Hill, 1935. H⁻ binding energy from J.-Z. Tang et al, *Phys. Rev.* **A 49**, 1021 (1994); Prof. Jackson found the paper for me.

We regard the single particle Hamiltonian

$$H_0 = \sum_i \left(\frac{\vec{p}_i^2}{2m} - \frac{Ze^2}{r_i} \right) \quad (9)$$

as the unperturbed and the Coulomb repulsion terms

$$\Delta H = \sum_{i < j} \frac{e^2}{r_{ij}} \quad (10)$$

as perturbation to the system.

Both of two electrons are put in the 1s orbitals. Therefore, the Slater determinant gives

$$|1s^2\rangle = \frac{1}{\sqrt{2}} [|1s^\uparrow 1s^\downarrow\rangle - |1s^\downarrow 1s^\uparrow\rangle]. \quad (11)$$

The unperturbed Hamiltonian has an eigenvalue on this state

$$H_0|1s^2\rangle = E_0|1s^2\rangle = 2 \left(-\frac{Z^2 e^2}{2a_B} \right) |1s^2\rangle. \quad (12)$$

This binding energy is too big compared to experimental values (see Table 1.

Now we add the 1st order correction in ΔH . All we need to do is to calculate the expectation value of ΔH in the unperturbed state:

$$\Delta E = \langle 1s^2 | \frac{e^2}{r_{12}} | 1s^2 \rangle. \quad (13)$$

Using the unperturbed wave function Eq. (11), we find

$$\begin{aligned} \Delta E = \frac{1}{2} & \left[\langle 1s^\uparrow 1s^\downarrow | \frac{e^2}{r_{12}} | 1s^\uparrow 1s^\downarrow \rangle - \langle 1s^\uparrow 1s^\downarrow | \frac{e^2}{r_{12}} | 1s^\downarrow 1s^\uparrow \rangle \right. \\ & \left. - \langle 1s^\downarrow 1s^\uparrow | \frac{e^2}{r_{12}} | 1s^\uparrow 1s^\downarrow \rangle + \langle 1s^\downarrow 1s^\uparrow | \frac{e^2}{r_{12}} | 1s^\downarrow 1s^\uparrow \rangle \right]. \quad (14) \end{aligned}$$

However, because ΔH commutes with the spin, the expression simplifies to

$$\Delta E = \frac{1}{2} \left[\langle 1s^\uparrow 1s^\downarrow | \frac{e^2}{r_{12}} | 1s^\uparrow 1s^\downarrow \rangle + \langle 1s^\downarrow 1s^\uparrow | \frac{e^2}{r_{12}} | 1s^\downarrow 1s^\uparrow \rangle \right]. \quad (15)$$

Finally, the spin part does not affect the expectation values, and we find

$$\Delta E = \langle 1s1s | \frac{e^2}{r_{12}} | 1s1s \rangle. \quad (16)$$

This is calculated by the integral

$$\Delta E = \frac{Z^6}{a_B^6} \int d\vec{x}_1 d\vec{x}_2 \frac{e^2}{r_{12}} (2e^{-Zr_1/a_B} Y_0^0(\theta_1, \phi_1))^2 (2e^{-Zr_2/a_B} Y_0^0(\theta_2, \phi_2))^2. \quad (17)$$

Because $Y_0^0 = 1/\sqrt{4\pi}$ and the only piece that depends on angles is $r_{12} = \sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos \theta_{12}}$, one can perform $\cos \theta_{12}$ integral and then r_1, r_2 integrals. But the following trick is useful when you evaluate similar integrals with different states. Use the identities

$$\frac{1}{r_{12}} = \sum_{l=0}^{\infty} \frac{r_{<}^l}{r_{>}^{l+1}} P_l(\cos \theta_{12}), \quad (18)$$

where $r_{<} = \min(r_1, r_2)$, $r_{>} = \max(r_1, r_2)$, $\cos \theta_{12} = (\vec{x}_1 \cdot \vec{x}_2)/r_1/r_2$, and

$$P_l(\cos \theta_{12}) = \frac{4\pi}{2l+1} \sum_{m=-l}^l Y_l^{m*}(\theta_1, \phi_1) Y_l^m(\theta_2, \phi_2). \quad (19)$$

Going back to Eq. (17), and replacing e^2/r_{12} using the identities Eq. (18,19), angular integrals in \vec{x}_1, \vec{x}_2 selects only $l = 0, m = 0$ piece in the summation. Therefore one finds

$$\Delta E = \frac{Z^6}{a_B^6} \int_0^\infty r_1^2 dr_1 r_2^2 dr_2 16 \frac{e^2}{r_{>}} e^{-2Z(r_1+r_2)} = \frac{5}{8} \frac{Z e^2}{a_B}. \quad (20)$$

Adding this energy to the single-particle energy Eq. (12), agreement between data and calculation is already quite good.

2.2 Variational Method

The variational method uses the theorem that the expectation value of the Hamiltonian in *any* state is larger than the ground-state energy eigenvalue. Therefore, one can try to minimize the expectation value using a trial wave function with respect to its parameters to get closer to the ground-state energy eigenvalue.

We apply this method to the Helium-like atoms discussed in the previous section. We take the trial wave function the same as before, expect that we choose

$$\psi_{1s}(\vec{x}) = \left(\frac{Z'}{a_B} \right)^{3/2} e^{-Z'r/a_B}. \quad (21)$$

The idea behind this choice that the presence of the other electron effectively *screens* the nuclear charge, resulting in a smaller Z' than the true Z . We calculate the expectation value of the Hamiltonian using this modified ψ_{1s} and minimize it with respect to Z' . Note that we do not change Z in the Hamiltonian because it is a physical quantity. Note also that the wave function is no longer an eigenstate of H_0 once $Z' \neq Z$. Barring these points in mind, the single particle piece is

$$\langle 1s | \frac{\vec{p}^2}{2m} - \frac{Z e^2}{r} | 1s \rangle = \frac{Z' e^2}{2a_B} - \frac{Z Z' e^2}{a_B}. \quad (22)$$

On the other hand, the calculation of the Coulomb repulsion is the same as before and we find

$$\langle 1s1s | \frac{e^2}{r_{12}} | 1s1s \rangle = \frac{5}{8} \frac{Z' e^2}{a_B}. \quad (23)$$

Therefore,

$$\langle 1s^2 | H | 1s^2 \rangle = \frac{e^2}{a_B} \left[2 \left(\frac{Z'^2}{2} - Z Z' \right) + \frac{5}{8} Z' \right]. \quad (24)$$

Now, we minimize this expression with respect to Z' , and find the minimum is at $Z' = Z - 5/16$, and

$$E_{\text{var}} = -\frac{e^2}{a_B} \frac{(16Z - 5)^2}{256}. \quad (25)$$

The values are shown in Table 1. The agreement between data and theory is further improved.

Obviously, the variational method can further be refined by using more and more complicated trial wave function. Hylleraas used a trial wave function with fourteen parameters, and obtained a result that differs from data only by 0.0016 eV. In fact, his calculated energy was *lower* than the data, in apparent contradiction to the principle of the variational method. The resolution is that, at this level of precision, one cannot trust the non-relativistic Hamiltonian Eq. (8) any more, and needs to include relativistic effects, spin-orbit coupling, etc. Because data of course includes all these additional effects, while Hylleraas used Eq. (8), his variational energy came out somewhat lower than the experimental energy.

3 Multi-Electron Atoms

As you go to atoms with more electrons, the perturbation theory becomes increasingly cumbersome. We can again start with the Slater determinant of single-particle states $|\lambda_1, \lambda_2, \dots, \lambda_N\rangle$. Each $|\lambda_i\rangle$ refers to a state $|n_i, l_i, m_i, s_i\rangle$. One can calculate the first-order perturbation in ΔH using the following decomposition:

$$E_0 = \sum_i E_{\lambda_i}, \quad (26)$$

$$\Delta E = \sum_{i < j} \left[\langle \lambda_i \lambda_j | \frac{e^2}{r_{ij}} | \lambda_i \lambda_j \rangle - \langle \lambda_i \lambda_j | \frac{e^2}{r_{ij}} | \lambda_j \lambda_i \rangle \right]. \quad (27)$$

Many of them trivially vanish because the perturbation commutes with spin. The term with two states exchanged is called “exchange energy.”

One of the important consequences of the perturbation is to lift the degeneracy among states with the same principal quantum number n . For instance, $2s$ and $2p$ states are degenerate. For hydrogen-like atoms, the degeneracy is lifted only by corrections of $O(\alpha^2)$ due to the relativistic effect

and the spin-orbit coupling. (It still leaves the degeneracy between $2s^{1/2}$ and $2p^{1/2}$, which is lifted by Lamb shift, a yet higher order effect.) However, in multi-electron atoms, the degeneracy is lifted by the Coulomb repulsion among electrons, which is a much larger effect.

As an example, consider three-electron atoms Li, Be^+ , B^{++} , etc. With the unperturbed (single-particle) Hamiltonian, 2 possible $|1s^2 2s\rangle$ states for two spin orientations and 6 possible $|1s^2 2p\rangle$ states for three $m = -1, 0, +1$ values with two spin orientations, are all degenerate. With only three electrons, it is simple enough to calculate the perturbation, and you find that $|1s^2 2p\rangle$ states are higher than $|1s^2 2s\rangle$ states. Degeneracy among $|1s^2 2p\rangle$ or $|1s^2 2s\rangle$ states still remain, because of separate conservation of L and S in the absence of the spin-orbit coupling. This leads to the well-known rule you learn in chemistry class that you should fill $2s$ states first and then move on to $2p$ states later on.

In general, higher l states have higher energies. This point is intuitively understood as follows. The highest $l = n - 1$ state corresponds to classical circular orbit, and lower l values are more eccentric. The lowest $l = 0$ state has zero ellipticity, *i.e.*, the particle moves only along the radial direction with no angular motion. (Of course, such a trajectory does not exist classically, but we are only talking about classical analogs! This point had apparently caused a lot of confusion in early days of quantum mechanics when people didn't consider $l = 0$ state because of the prejudice from classical mechanics.) Therefore lower l states probe more of inner part of the atom, while the higher l states stay in the outer parts. The other electrons surrounding the nucleus screen its electric charge, and the effect of screening is more important at larger radii. Therefore the higher l states see the nuclear charge more screened, and hence they are less bound. This argument qualitatively explains why higher l states have higher energies due to the Coulomb repulsion among electrons.

4 Self-Consistent Field Method

The discussion in the previous section suggests that the dominant effect of the Coulomb repulsion among electrons is to modify the nuclear Coulomb potential by screening effect. Therefore, one can hope that, with an appropriate modification of the Coulomb potential, we can incorporate the bulk of the Coulomb repulsion effects while still using the language of single-particle

states. This is the idea of the mean-field method, or self-consistent field method.

There are at least two self-consistent field methods for multi-electron atoms. One of them is based on semi-classical and statistical arguments, called Thomas–Fermi model. The other more rigorous one is Hartree–Fock model. We discuss them in order.

4.1 Thomas–Fermi Model

The Thomas–Fermi model is based on the semi-classical statistical argument valid for a large number of electrons. If you fill up all the states up to the Fermi level, by definition, the number of states below the Fermi level equals the number of electrons. Given a mean-field potential, the number of states is given by the size of the phase space volume in the unit of $(2\pi\hbar)^3$. On the other hand, the number density of electrons determined this way should reproduce the assumed mean-field potential. Putting them together one finds a solution to the system. A spherical symmetry is assumed throughout the discussions.

Suppose a distribution of electrons with the number density $\rho(r)$. For the total number of electrons N ,

$$N = 4\pi \int \rho(r)r^2 dr. \quad (28)$$

The distribution of electron determines the Coulomb potential ϕ according to the Poisson equation

$$\Delta\phi = \frac{1}{r} \frac{d^2}{dr^2} r\phi = 4\pi e\rho(r) - 4\pi Ze\delta(\vec{x}). \quad (29)$$

Since the delta function has a support only at the origin, we can solve the equation

$$\frac{1}{r} \frac{d^2}{dr^2} r\phi = 4\pi e\rho(r) \quad (30)$$

and impose the boundary condition

$$\lim_{r \rightarrow 0} r\phi(r) = Ze \quad (31)$$

instead. Here, we allowed for the possibility that the number of electrons N is different from the nuclear charge Z , *i.e.*, ions. For neutral atoms $N = Z$. The

physical reason behind the boundary condition is obvious: close to the origin, the only charge inside the radius is that of the nucleus, and the Coulomb potential is given only by the nucleus so that $\phi(r) \approx Ze/r$. More formal way of deriving it is by using the normalization

$$\begin{aligned}
Ne &= 4\pi e \int_0^\infty dr r^2 \rho(r) \\
&= \int_0^\infty dr r \frac{d^2}{dr^2} r\phi \\
&= \left[r \frac{d}{dr} r\phi \right]_0^\infty - \int_0^\infty dr \frac{d}{dr} r\phi \\
&= 0 - [r\phi]_0^\infty \\
&= -(Z - N)e + (r\phi(r))|_{r \rightarrow 0}.
\end{aligned} \tag{32}$$

In the last line, we used the fact that the total charge of the system is $(Z - N)e$ and hence the Coulomb potential at infinity must be given by $(Z - N)e/r$.

Of course the potential energy for an electron is given by

$$V(r) = -e\phi(r). \tag{33}$$

The Poisson equation determines the potential in terms of the distribution. We need now to determine the distribution in terms of the potential to find a self-consistent solution. At a given position r , the number density can be estimated by the following semi-classical statistical argument. It is assumed that all states up to the Fermi energy ε_F are filled. Note that there are 2 states for each spin in a phase space volume in the unit of $(2\pi\hbar)^3$ in the semi-classical limit. Then the number density in the phase space is given by

$$n(\vec{r}, \vec{p}) = \begin{cases} \frac{2}{(2\pi\hbar)^3} & \text{for } \frac{\vec{p}^2}{2m} - e\phi < \varepsilon_F \\ 0 & \text{for } \frac{\vec{p}^2}{2m} - e\phi > \varepsilon_F \end{cases} \tag{34}$$

From this point on, we define Φ by

$$e\Phi = e\phi + \varepsilon_F \tag{35}$$

so that the number density is written as

$$n(\vec{r}, \vec{p}) = \begin{cases} \frac{2}{(2\pi\hbar)^3} & \text{for } \frac{\vec{p}^2}{2m} - e\Phi < 0 \\ 0 & \text{for } \frac{\vec{p}^2}{2m} - e\Phi > 0 \end{cases} \tag{36}$$

Φ still satisfies the same Poisson equation Eq. (29) because a constant disappears under the Laplacian Δ and the same boundary condition Eq. (31).

To obtain the number density in space $\rho(r)$, we integrate the phase space density in the momentum space. To satisfy the conditions in Eq. (36), the phase space density is constant $2/(2\pi\hbar)^3$ up to $p = (2me\Phi)^{1/2}$ and hence

$$\rho(r) = \begin{cases} \frac{2}{(2\pi\hbar)^3} \frac{4\pi}{3} (2me\Phi)^{3/2} & (e\Phi > 0) \\ 0 & (e\Phi < 0) \end{cases}. \quad (37)$$

Therefore we now try to solve coupled equations Eq. (29) and Eq. (37) under the boundary condition Eq. (31). This is done in a Z -independent way by introducing variable x by

$$r = Z^{-1/3}bx, \quad b = \frac{1}{2} \left(\frac{3\pi}{4} \right)^{2/3} \frac{\hbar^2}{me^2} \simeq 0.5 \text{ \AA}, \quad (38)$$

and a new function χ defined by

$$\Phi(r) = \frac{Ze}{r} \chi(r). \quad (39)$$

The meaning of the function $\chi(r)$ is the degree how much the nuclear charge is screened by the surrounding electrons. Then the number density is rewritten as

$$\rho(r) = \begin{cases} \frac{Z^2}{4\pi b^3} \left(\frac{\chi}{x} \right)^{3/2} & (\chi > 0) \\ 0 & (\chi < 0) \end{cases}. \quad (40)$$

The Poisson equation Eq. (29) then reads as

$$\frac{d^2\chi}{dx^2} = \begin{cases} x^{-1/2}\chi^{3/2} & (\chi > 0) \\ 0 & (\chi < 0) \end{cases}. \quad (41)$$

We solve this equation under the boundary condition $\chi(0) = 1$. What is the required behavior of $\chi(x)$ at $x \rightarrow \infty$? To see this, we first note that the second derivative χ'' is always positive or zero, and hence the function is convex. It means that if $\chi(x)$ crosses zero, it does so only once. Let us call the position of the zero x_0 . Since $\rho > 0$ only for $\chi > 0$ (see Eq. (40)), all electrons are inside the radius x_0 . Therefore the total number of electrons is

$$\begin{aligned} N &= \int_0^{Z^{-1/3}bx_0} 4\pi r^2 dr \frac{Z^2}{4\pi b^3} \left(\frac{\chi}{x} \right)^{3/2} = Z \int_0^{x_0} dx x \chi(x)'' \\ &= Z[x\chi' - \chi]_0^{x_0} = Z[x_0\chi'(x_0) + 1]. \end{aligned} \quad (42)$$

When $N = Z$, $\chi'(x_0) = 0$. If x_0 were finite, $\chi(x)$ hits zero with a finite slope and $\chi'(x_0)$ cannot vanish. Therefore a neutral atoms require that $x_0 = \infty$, *i.e.*, $\chi(x)$ approaches zero at infinity. This dictates a particular value of $\chi'(0) = -1.588070845$ to solve the differential equation numerically.

A technical remark. When you solve the differential equation Eq. (41) numerically, one needs to avoid the singularity $1/\sqrt{x}$. One way to do so is to first notice that $\chi(x) = 1 + \frac{4}{3}x^{3/2}$ solves the equation at the origin together with $\chi(0) = 1$. One can write

$$\chi(x) = \left(1 + \frac{4}{3}x^{3/2}\right)y(x),$$

and rewrite the differential equation as

$$\left(1 + \frac{4}{3}x^{3/2}\right)y''(x) + 4x^{1/2}y'(x) + \frac{1}{x^{1/2}}y(x) \left[1 - \left(1 + \frac{4}{3}x^{3/2}\right)^{3/2}y(x)^{1/2}\right] = 0.$$

Because the behavior of $y(x)$ at the origin is $1 + \chi'(0)x + O(x^{3/2})$, the factor in the square bracket vanishes as $O(x)$ and hence the whole equation is regular. This can be put in Mathematica, with an **If** statement to make the factor in the square bracket vanish at $x = 0$, and you can choose values of $\chi'(0)$ by trial and error to find a solution that goes smoothly to zero at the infinity.

When $N < Z$ (positive ions), however, $x_0\chi'(x_0) = -(Z - N)/Z$ and hence $\chi(x)$ hits zero at a finite x_0 . Beyond x_0 , $\chi'' = 0$ and hence

$$\chi(x) = (x - x_0)\chi'(x_0) = -\frac{r - r_0}{r_0} \frac{Z - N}{Z}, \quad (43)$$

where $r_0 = Z^{-1/3}bx_0$. Therefore the Coulomb potential is

$$e\phi = e\Phi - \varepsilon_F = -\frac{Ze^2}{r} \frac{r - r_0}{r_0} \frac{Z - N}{Z} - \varepsilon_F = \frac{(Z - N)e^2}{r} - \frac{(Z - N)e^2}{r_0} - \varepsilon_F. \quad (44)$$

Because there are no electrons beyond r_0 and hence the Coulomb potential must be simply $\phi = (Z - N)e/r$, we find the Fermi energy

$$\varepsilon_F = -\frac{(Z - N)e}{r_0}. \quad (45)$$

The solution is obtained by $\chi(x)$ with $\chi'(x_0) < -1.588070845$ so that $x_0\chi'(x_0) = -(Z - N)/Z$.

Thomas–Fermi model is a crude model based on semi-classical argument and statistical treatment, but is not so bad in practice. In Figs. 6,7,8, we will

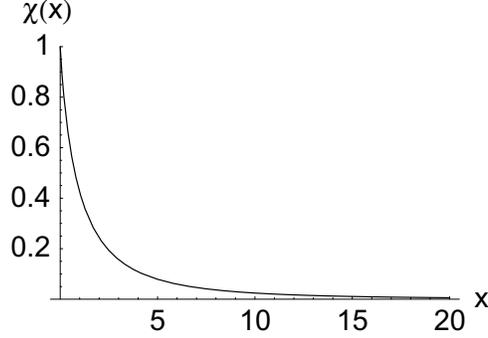


Figure 1: Numerical calculation of $\chi(x)$ for neutral atoms.

show the comparison between the Thomas–Fermi model and more detailed Hartree–Fock–Slater model as described next for the ionization energies of electrons in given orbitals. HFS model is known to agree with data at a few percent level.

With the Thomas–Fermi model, we can calculate the total binding energy of neutral atoms that can be compared to the data. Because the number density of electrons is non-zero only for $\frac{p^2}{2m} < e\Phi = \frac{Ze^2}{r}\chi$, or $|\vec{p}| < \sqrt{2me\Phi(r)}$, we can obtain the kinetic energy by the phase space integral

$$\begin{aligned} E_K &= 2 \int \frac{d\vec{p}d\vec{x}}{(2\pi\hbar)^3} \frac{p^2}{2m} \theta(\sqrt{2me\Phi(r)} - p) \\ &= \frac{1}{5(2\pi\hbar)^3 m} \int_0^\infty dr (2me\Phi(r))^{5/2}. \end{aligned} \quad (46)$$

Plugging in $\Phi = \frac{Ze}{r}\chi$, and changing the integration variable $r = Z^{-1/3}bx$, we find

$$E_K = \frac{3}{5} \frac{Z^{7/3}e^2}{b} \int_0^\infty dx \frac{\chi^{5/2}}{x^{1/2}}. \quad (47)$$

Using the differential equation $\chi'' = \chi^{3/2}/x^{1/2}$ and the boundary conditions, $\chi(0) = 1$ and $\chi(\infty) = 0$, we can perform this integration analytically. We first note

$$\begin{aligned} \int_0^\infty \frac{\chi^{5/2}}{x^{1/2}} dx &= \int_0^\infty \chi \frac{\chi^{3/2}}{x^{1/2}} dx = \int_0^\infty \chi'' \chi dx \\ &= [\chi\chi']_0^\infty - \int_0^\infty \chi' \chi' dx = -\chi'(0) - \int_0^\infty \chi'^2 dx. \end{aligned} \quad (48)$$

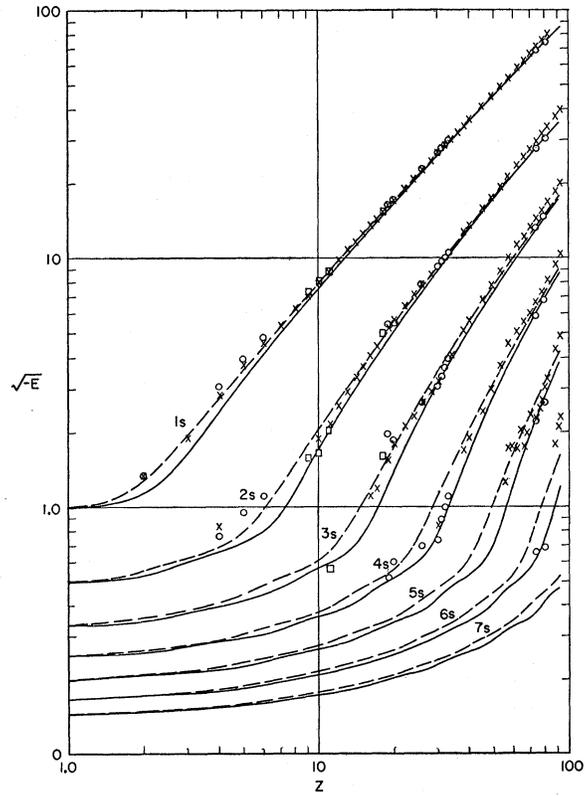


FIG. 9. The square root of the computed s -levels are shown with the solid line for the Thomas-Fermi atom and with the dashed line for the Thomas-Fermi-Dirac atom. The circles (\circ) are the values computed by the Hartree method; the squares (\square) are the values computed by the Hartree-Fock method. The crosses (\times) are the experimental values.

Figure 2: Comparison of Thomas-Fermi, Thomas-Fermi-Dirac calculations to data from Richard Latter, *Phys. Rev.* **99**, 510 (1955).

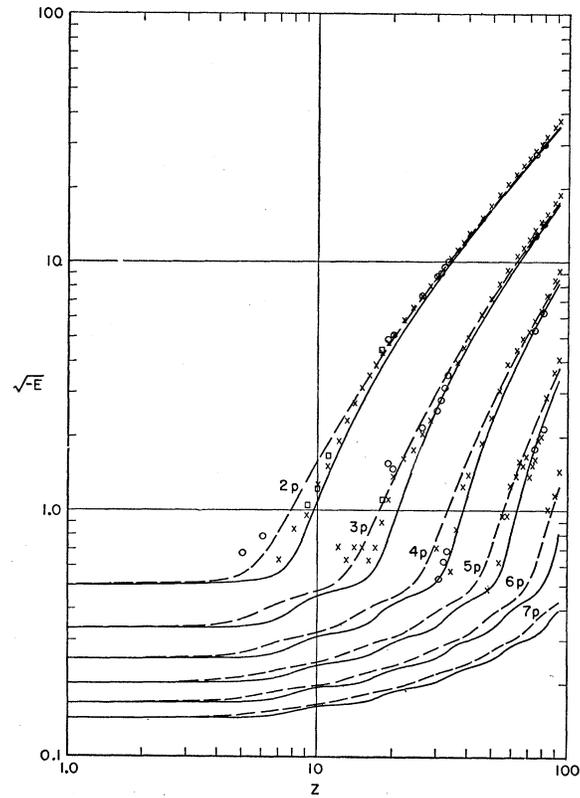


FIG. 10. The square root of the computed p -levels are shown with the solid line for the Thomas-Fermi atom and with the dashed line for the Thomas-Fermi-Dirac atom. The circles (O) are the values computed by the Hartree method; the squares (□) are the values computed by the Hartree-Fock method. The crosses (X) are the experimental values where the doublet energies have been averaged.

Figure 3: Comparison of Thomas-Fermi, Thomas-Fermi-Dirac calculations to data from Richard Latter, *Phys. Rev.* **99**, 510 (1955).

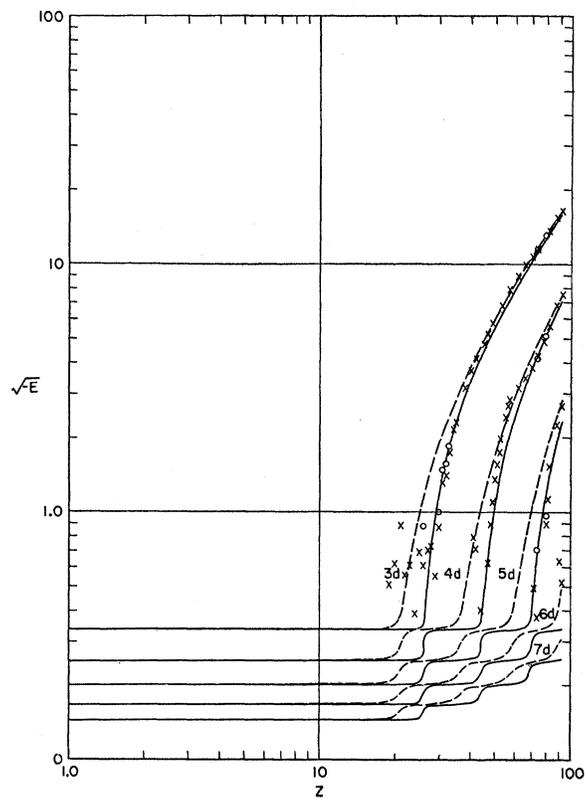


FIG. 11. The square root of the computed d -levels are shown with the solid line for the Thomas-Fermi atom and with the dashed line for the Thomas-Fermi-Dirac atom. The circles (O) are the values computed by the Hartree method; the squares (□) are the values computed by the Hartree-Fock method. The crosses (X) are the experimental values where the doublet energies have been averaged.

Figure 4: Comparison of Thomas-Fermi, Thomas-Fermi-Dirac calculations to data from Richard Latter, *Phys. Rev.* **99**, 510 (1955).

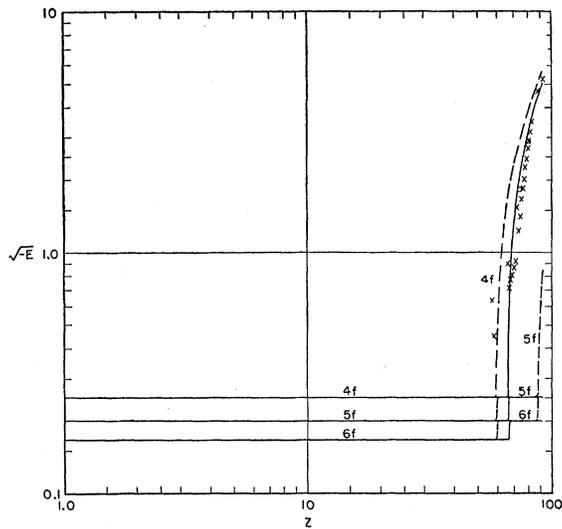


FIG. 12. The square root of the computed f -levels are shown with the solid line for the Thomas-Fermi atom and with the dashed line for the Thomas-Fermi-Dirac atom. The circles (O) are the values computed by the Hartree method; the squares (□) are the values computed by the Hartree-Fock method. The crosses (X) are the experimental values where the doublet energies have been averaged.

Figure 5: Comparison of Thomas-Fermi, Thomas-Fermi-Dirac calculations to data from Richard Latter, *Phys. Rev.* **99**, 510 (1955).

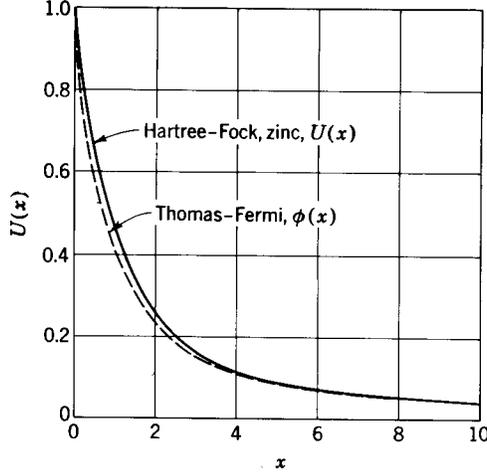


Fig. 16-2. Thomas-Fermi function ϕ as function of x , compared with corresponding self-consistent-field function $U(x)$ from Fig. 7-1, for zinc.

Figure 6: Comparison of the screening function between Thomas-Fermi and Hartree-Fock-Slater methods. Taken from "Quantum Theory of Matter," by John C. Slater, McGraw-Hill, 1968.

On the other hand, there is another way to do the integration by parts,

$$\begin{aligned}
 \int_0^\infty \frac{\chi^{5/2}}{x^{1/2}} dx &= [2x^{1/2}\chi^{5/2}]_0^\infty - \int_0^\infty 2x^{1/2} \frac{5}{2} \chi^{3/2} \chi' dx \\
 &= -5 \int_0^\infty x^{1/2} \chi^{3/2} \chi' dx = -5 \int_0^\infty x \chi'' \chi' dx = -5 \int_0^\infty x \frac{d}{dx} \frac{1}{2} \chi'^2 dx \\
 &= -5 \left\{ \left[x \frac{1}{2} \chi'^2 \right]_0^\infty - \int_0^\infty \frac{1}{2} \chi'^2 dx \right\} = \frac{5}{2} \int_0^\infty \chi'^2 dx. \tag{49}
 \end{aligned}$$

Comparing Eqs. (48,49), we find

$$\int_0^\infty \frac{\chi^{5/2}}{x^{1/2}} dx = -\frac{5}{7} \chi'(0) > 0, \quad \int_0^\infty \chi'^2 dx = -\frac{2}{7} \chi'(0) > 0. \tag{50}$$

Therefore, we find

$$E_K = \frac{3}{7} \frac{Z^{7/3} e^2}{b} (-\chi'(0)). \tag{51}$$

The potential energy between the electron and the nucleus is

$$E_{eA} = - \int d\vec{r} \rho(r) \frac{Ze^2}{r} = -\frac{Z^{7/3} e^2}{b} \int_0^\infty dx \frac{\chi^{3/2}}{x^{1/2}}$$

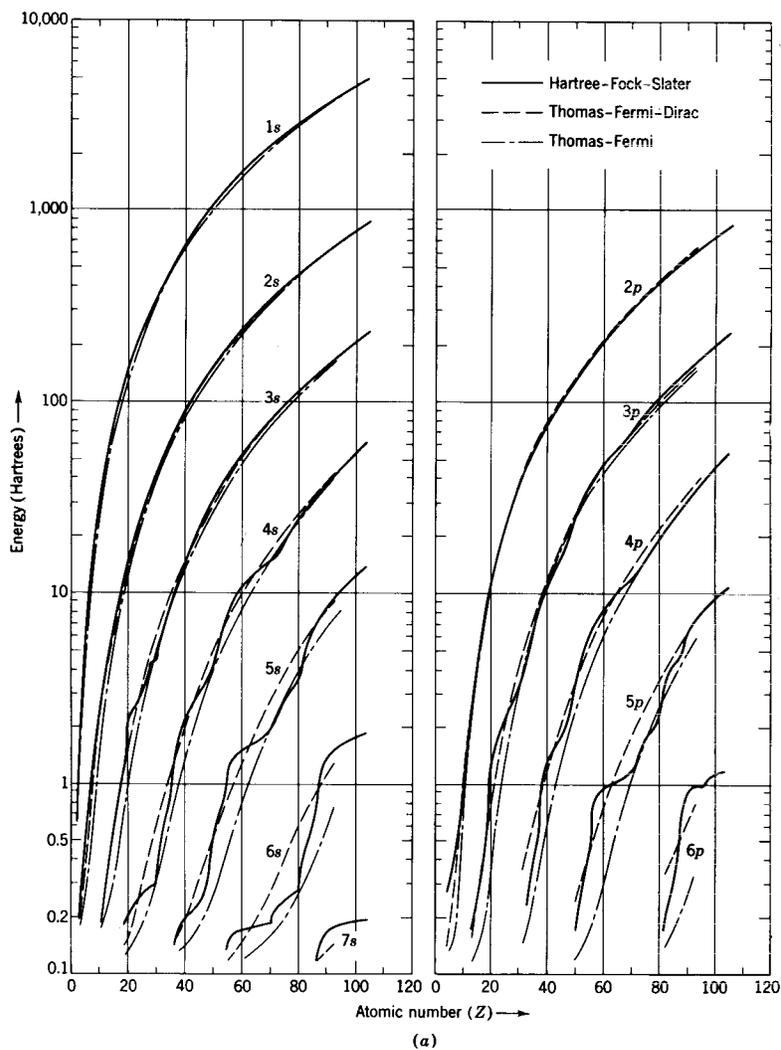


Fig. 16-3. One-electron energies of atoms, calculated by solving Schrödinger's equation in the Thomas-Fermi potential, compared with Herman and Skillman's (*op. cit.*) calculated one-electron energies.

Figure 7: Comparison of ionization energies calculated with Thomas-Fermi model, Thomas-Fermi-Dirac model, and Hartree-Fock-Slater model. Taken from "Quantum Theory of Matter," by John C. Slater, McGraw-Hill, 1968.

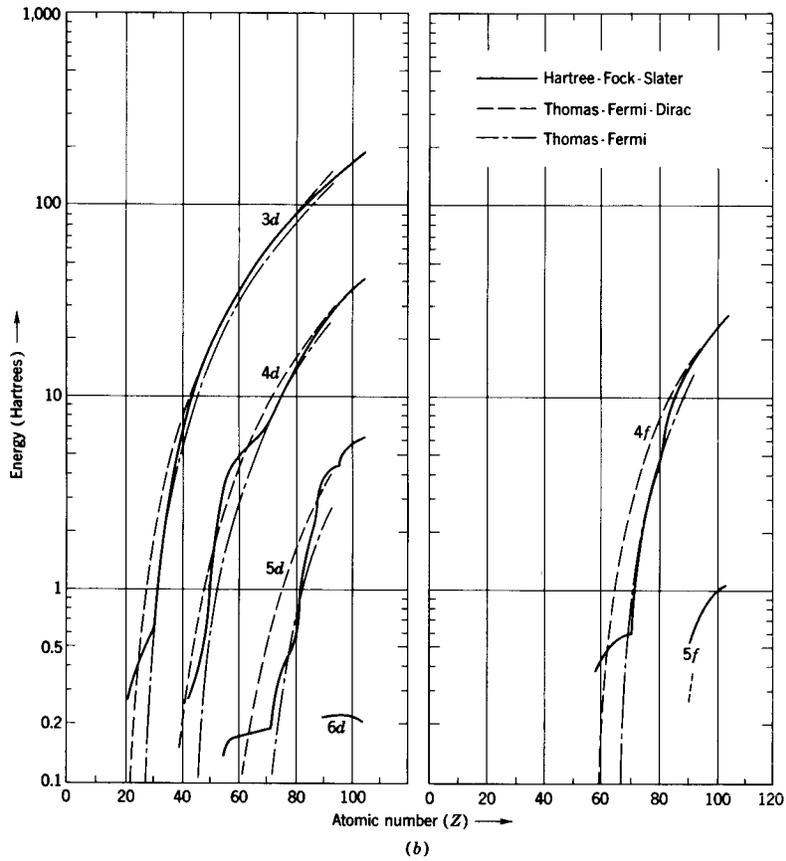


Fig. 16-3.

Figure 8: Comparison of ionization energies calculated with Thomas-Fermi model, Thomas-Fermi-Dirac model, and Hartree-Fock-Slater model. Taken from "Quantum Theory of Matter," by John C. Slater, McGraw-Hill, 1968.

$$= -\frac{Z^{7/3}e^2}{b} \int_0^\infty \chi'' dx = -\frac{Z^{7/3}e^2}{b} [\chi'(x)]_0^\infty = -\frac{Z^{7/3}e^2}{b} (-\chi'(0)). \quad (52)$$

Finally, the electron-electron Coulomb (positive) energy is given by

$$E_{ee} = \frac{1}{2} \int d\vec{r}_1 d\vec{r}_2 \rho(r_1) \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} \rho(r_2). \quad (53)$$

Using the multipole expansion of the Coulomb potential, we find only the $l = 0$ contributes due to the spherical symmetry of the electron number density $\rho(r)$. Therefore,

$$\begin{aligned} E_{ee} &= \frac{1}{2} \int r_1^2 dr_1 d\Omega_1 r_2^2 dr_2 d\Omega_2 \rho(r_1) \rho(r_2) \frac{e^2}{r_>} 4\pi Y_0^0(\Omega_1) Y_0^0(\Omega_2) \\ &= e^2 (4\pi)^2 \int_0^\infty dr_1 r_1^2 \int_0^{r_1} dr_2 r_2^2 \rho(r_1) \rho(r_2) \frac{1}{r_1}. \end{aligned} \quad (54)$$

Now changing the variables to $x_{1,2}$,

$$E_{ee} = \frac{Z^{7/3}e^2}{b} \int_0^\infty dx_1 \frac{\chi(x_1)^{3/2}}{x_1^{1/2}} \int_0^{x_1} x_2^{1/2} \chi(x_2)^{3/2}. \quad (55)$$

Using the differential equation $\chi'' = \chi^{3/2}/x^{1/2}$, it simplifies to

$$E_{ee} = \frac{Z^{7/3}e^2}{b} \int_0^\infty dx_1 \chi''(x_1) \int_0^{x_1} x_2 \chi''(x_2). \quad (56)$$

Integrating in parts in x_1 ,

$$E_{ee} = \frac{Z^{7/3}e^2}{b} \left\{ \left[\chi'(x_1) \int_0^{x_1} dx_2 x_2 \chi''(x_2) \right]_0^\infty + \int_0^\infty dx_1 \chi'(x_1) x_1 \chi''(x_1) \right\}. \quad (57)$$

The first term in the curly braces vanishes at the boundaries, while the second term can be integrated in parts again (relabeling $x = x_1$),

$$\begin{aligned} E_{ee} &= \frac{Z^{7/3}e^2}{b} \left\{ - \left[x \frac{1}{2} \chi'(x)^2 \right]_0^\infty + \int_0^\infty dx \frac{1}{2} \chi'(x)^2 \right\} \\ &= \frac{Z^{7/3}e^2}{2b} \int_0^\infty \chi'(x)^2. \end{aligned} \quad (58)$$

Using Eq. (50),

$$E_{ee} = \frac{1}{7} \frac{Z^{7/3}e^2}{b} (-\chi'(0)). \quad (59)$$

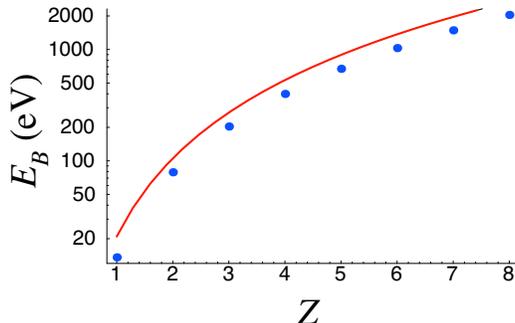


Figure 9: The comparison of the total binding energy of neutral atoms between the Thomas–Fermi model (solid line) and data (dots) taken from J. F. Barnes and R. D. Cowan, *Phys. Rev.* **132**, 236-240 (1963).

Putting Eqs. (51,52,59) together, we find the binding energy,

$$E_B = |E_K + E_{eA} + E_{ee}| = \frac{3}{7} \frac{Z^{7/3} e^2}{b} (-\chi'(0)) = 20.9 \text{ eV} Z^{7/2}. \quad (60)$$

It is noteworthy that the virial theorem holds, $E_{eA} + E_{ee} = -2E_K$. This result compares well with the data, given how crude the model is.

4.2 Hartree–Fock Model

A better method which does not rely on the statistical semi-classical argument but still depends on the individual particle approximation and hence ignores correlations in the wave function is the Hartree–Fock method. This model is supposed to give the best variational wave function within the individual particle approximation.

The basic idea is the self-consistency, as in the Thomas–Fermi model. The difference is that instead of using a smooth semi-classical electron number density $\rho(r)$, we study the single-particle wave functions.

We take a trial wave function in terms of a Slater determinant

$$|\Psi\rangle = \frac{1}{\sqrt{N!}} \det \begin{pmatrix} |\psi_1(1)\rangle & |\psi_1(2)\rangle & \cdots & |\psi_1(N)\rangle \\ |\psi_2(1)\rangle & |\psi_2(2)\rangle & \cdots & |\psi_2(N)\rangle \\ \vdots & \vdots & \ddots & \vdots \\ |\psi_N(1)\rangle & |\psi_N(2)\rangle & \cdots & |\psi_N(N)\rangle \end{pmatrix}. \quad (61)$$

The notation here is that $|\psi_i(j)\rangle$ is a state where the particle j occupies the state i . The Hamiltonian is the same as before Eq. (8), and the expectation value of the Hamiltonian is given by

$$\begin{aligned}
E &= \langle \Psi | H | \Psi \rangle \\
&= \sum_i \langle \psi_i | \left(\frac{\vec{p}^2}{2m} - \frac{Ze^2}{r} \right) | \psi_i \rangle \\
&\quad + \sum_{i < j} \left[\langle \psi_i(1)\psi_j(2) | \frac{e^2}{r_{12}} | \psi_i(1)\psi_j(2) \rangle - \langle \psi_i(1)\psi_j(2) | \frac{e^2}{r_{12}} | \psi_j(1)\psi_i(2) \rangle \right].
\end{aligned} \tag{62}$$

From this expression, we take the variation with respect to single particle states $|\psi_i\rangle$. Note that we can regard the variation of the ket $|\psi_i\rangle$ and the bra $\langle \psi_i|$ independently because they are both complex. Taking the variation of the expectation value E with the bra $\langle \psi_i|$,

$$\begin{aligned}
\delta E &= (\delta \langle \psi_i |) \left(\frac{\vec{p}^2}{2m} - \frac{Ze^2}{r} \right) | \psi_i \rangle \\
&\quad + \sum_{j \neq i} (\delta \langle \psi_i(1) |) \left[\langle \psi_j(2) | \frac{e^2}{r_{12}} | \psi_i(1)\psi_j(2) \rangle - \langle \psi_j(2) | \frac{e^2}{r_{12}} | \psi_j(1)\psi_i(2) \rangle \right].
\end{aligned} \tag{63}$$

Here, we used the fact that the sum $\sum_{i < j}$ is the same as $\frac{1}{2} \sum_{i \neq j}$, and then that the variation with respect to i and j give the same contribution to reduce the sum to $\sum_{i \neq j}$.

However, the above variation missed the important fact that we need to preserve the orthonormality of the set of single particle states $|\psi_i\rangle$. In order to do so, we use Lagrange multiplier method

$$\delta [E - \lambda_{ij} (\langle \psi_i | \psi_j \rangle - \delta_{ij})] = 0, \tag{64}$$

where λ_{ij} are the Lagrange multipliers. Note that $\lambda_{ij} = \lambda_{ji}^*$ because of the property $\langle \psi_i | \psi_j \rangle = \langle \psi_j | \psi_i \rangle^*$ and hence they form a hermitean matrix. Therefore, the variational method gives the condition

$$\begin{aligned}
&\left(\frac{\vec{p}^2}{2m} - \frac{Ze^2}{r} \right) | \psi_i \rangle \\
&+ \sum_{j \neq i} \left[\langle \psi_j(2) | \frac{e^2}{r_{12}} | \psi_i(1)\psi_j(2) \rangle - \langle \psi_j(2) | \frac{e^2}{r_{12}} | \psi_j(1)\psi_i(2) \rangle \right] - \lambda_{ij} | \psi_j \rangle = 0.
\end{aligned} \tag{65}$$

The term in the square bracket with i and j interchanged is called the exchange term. Now we rewrite this equation in the position space. Taking the inner product of this equation with the position eigenbra $\langle \vec{x} |$, we find

$$\begin{aligned} & \left(-\frac{\hbar^2 \Delta}{2m} - \frac{Ze^2}{r} \right) \psi_i(\vec{x}) \\ & + \sum_{j \neq i} \int d\vec{y} \psi_j(\vec{y})^* \left[\frac{e^2}{|\vec{x} - \vec{y}|} \psi_j(\vec{y}) \psi_i(\vec{x}) - \frac{e^2}{|\vec{x} - \vec{y}|} \psi_i(\vec{y}) \psi_j(\vec{x}) \delta_{m_{si}, m_{sj}} \right] \\ & = \lambda_{ij} \psi_j(\vec{x}). \end{aligned} \quad (66)$$

This is the Hartree–Fock equation. An important point here is that the second term in the square bracket survives only when the state i and j have the same spin. Now, note that λ_{ij} form a hermitean matrix, and we can always go to the basis of single particle states where the matrix λ_{ij} is diagonal with real eigenvalues, $\lambda_{ij} = \delta_{ij} \lambda_i$, without a loss of generality. We always use such a basis hereafter. Then the r.h.s. of Eq. (66) is simply $\lambda_i \psi_i(\vec{x})$ and the Hartree-Fock equation becomes basically an eigenvalue equation for the single-particle states. Note also that the summation $\sum_{j \neq i}$ can include $j = i$ without changing the equation because the portion $j = i$ is subtracted by the exchange term. Without this trick, we had to solve the eigenvalue equation with different differential operator for each state ψ_i , but this trick makes the equation the same for all i ,

$$\left(-\frac{\hbar^2 \Delta}{2m} - \frac{Ze^2}{r} \right) \psi_i(\vec{x}) + V_{ee}(\vec{x}) \psi_i(\vec{x}) - \int d\vec{y} V_{ee}^{ex}(\vec{x}, \vec{y}) \psi_i(\vec{y}) = \lambda_i \psi_i(\vec{x}), \quad (67)$$

with

$$V_{ee}(\vec{x}) = \int d\vec{y} \frac{e^2}{|\vec{x} - \vec{y}|} \sum_j |\psi_j(\vec{y})|^2 \quad (68)$$

is the Coulomb potential for all electrons in the atom, and

$$V_{ee}^{ex} = \sum_j \frac{e^2}{|\vec{x} - \vec{y}|} \psi_j^*(\vec{y}) \psi_j(\vec{x}) \delta_{m_{si}, m_{sj}} \quad (69)$$

is the exchange term. Eq. (67) can now be regarded an eigenvalue equation similar to conventional Schrödinger equations except that it has a non-local potential term V_{ee}^{ex} . Except this non-local term, it has a mean-field potential

$$V_C(\vec{x}) = -\frac{Ze^2}{r} + \int d\vec{y} \frac{e^2}{|\vec{x} - \vec{y}|} \rho(\vec{y}) \quad (70)$$

for every state $\psi_i(\vec{x})$, where V_{ee} is determined by $\psi_i(\vec{x})$ as in Eq. (68) and hence is a self-consistent field. This equation can be solved numerically by iterative method. First, one take an ansatz for the self-consistent field $V_C(\vec{x})$, solves the eigenvalue equation Eq. (67), and use the solutions to re-evaluate the self-consistent field V_C . In general the result is different from the original ansatz, and you solve the eigenvalue equation again. You keep doing it until the input self-consistent field and the output self-consistent field are close enough within the predefined accuracy. For many atoms and simple molecules, the Hartree–Fock method is used extensively to work out energy levels and electronic structures.

4.3 Slater’s Approximation to the Exchange Term

The exchange term, however, complicates the analysis. Hartree, when he originally proposed this method, did not know the need for anti-symmetrizing the wave function, and his equation did not have the exchange term. Such an equation is called Hartree equation. However, we cannot ignore the exchange term. Slater later introduced another method to simplify the exchange term based on the Fermi-liquid approximation of the electronic states. The assumption is that one can evaluate the exchange term using the plane wave states instead of true single-particle wave functions in a given atom. Using the plane wave

$$\psi_i(\vec{x}) = \frac{1}{\sqrt{V}} e^{i\vec{k}_i \cdot \vec{x}}, \quad (71)$$

where V is the volume introduced to normalized the wave function and \vec{k}_i the wave vector, we can evaluate the exchange integral

$$\int d\vec{y} \psi_j(\vec{y})^* \frac{e^2}{|\vec{x} - \vec{y}|} \psi_j(\vec{x}) \psi_i(\vec{y}) = \frac{1}{V} \frac{4\pi e^2}{|\vec{k}_i - \vec{k}_j|^2} \psi_i(\vec{x}). \quad (72)$$

Then we sum over j to estimate exchange term as $\sum_j = \frac{2}{(2\pi)^3} V \int_0^{k_F} d\vec{k}_j$, where the numerator 2 is the spin degrees of freedom. To obtain the number density $\rho = N/V$, the integral goes up to the Fermi momentum $p_F = \hbar k_F$ such that

$$\rho = \frac{N}{V} = \frac{2}{(2\pi)^3} \frac{4\pi}{3} k_F^3. \quad (73)$$

Going back to Eq. (72) and performing the integral,

$$\sum_j \int d\vec{y} \psi_j(\vec{y})^* \frac{e^2}{|\vec{x} - \vec{y}|} \psi_j(\vec{x}) \psi_i(\vec{y}) \delta_{m_{s_i}, m_{s_j}}$$

$$= \frac{1}{(2\pi)^3} V \int_0^{k_F} d\vec{k}_j \frac{1}{V} \frac{4\pi e^2}{|\vec{k}_i - \vec{k}_j|^2} \psi_j(\vec{x}) = e^2 \frac{k_F}{2\pi} 4F(\eta) \psi_j(\vec{x}), \quad (74)$$

where

$$F(\eta) = \frac{1}{2} + \frac{1 - \eta^2}{4\eta} \ln \frac{1 + \eta}{1 - \eta} \quad (75)$$

for $\eta = |\vec{k}_i|/k_F$. The function $F(\eta)$ takes values between $F(0) = 1$ and $F(1) = 1/2$. This term corrects for the fact that the anti-symmetry of the fermionic wave function “repels” other electrons from the vicinity of the electron of the interest (“Fermi hole”) and the mean-field potential Eq. (70) must be correspondingly corrected to

$$V_C(\vec{x}) = -\frac{Ze^2}{r} + \int d\vec{y} \frac{e^2}{|\vec{x} - \vec{y}|} \rho(\vec{y}) - e^2 \left(\frac{3}{8\pi} \rho(\vec{x}) \right)^{1/3} 4F(\eta). \quad (76)$$

Finally, $F(\eta)$ is taken at its average value

$$F(\eta)_{\text{average}} = \frac{\int_0^1 \eta^2 F(\eta) d\eta}{\int_0^1 \eta^2 d\eta} = \frac{3}{4} \quad (77)$$

and we find

$$V_C(\vec{x}) = -\frac{Ze^2}{r} + \int d\vec{y} \frac{e^2}{|\vec{x} - \vec{y}|} \rho(\vec{y}) - 3e^2 \left(\frac{3}{8\pi} \rho(\vec{x}) \right)^{1/3}. \quad (78)$$

This is the Hartree–Fock–Slater (HFS) approximation. There is also a school which prefers $F(\eta)_{\text{min}} = 1/2$ instead of $3/4$. This may be called HFS’.

4.4 Comparison to Experiments

In order to compare Hartree–Fock results to experiments, we need to figure out the physical meaning of the eigenvalues λ_i . Going back to Eq. (66) for diagonal λ_i , we take inner product with $\langle \psi_i |$ and sum over i :

$$\begin{aligned} & \sum_i \langle \psi_i | \left(\frac{\vec{p}^2}{2m} - \frac{Ze^2}{r} \right) | \psi_i \rangle \\ & + \sum_{i,j} \left[\langle \psi_i(1)\psi_j(2) | \frac{e^2}{r_{12}} | \psi_i(1)\psi_j(2) \rangle - \langle \psi_i(1)\psi_j(2) | \frac{e^2}{r_{12}} | \psi_j(1)\psi_i(2) \rangle \right] = \sum_i \lambda_i. \end{aligned} \quad (79)$$

| | HF | HFS | HFS' | Observed |
|------|---------|---------|---------|----------|
| 1s | 118.606 | 117.830 | 118.678 | 117.85 |
| 2s | 12.321 | 11.901 | 12.345 | 12.15 |
| 2p | 9.571 | 9.125 | 9.607 | 9.15 |
| 3s | 1.277 | 1.146 | 1.292 | 1.074 |
| 3p | 0.591 | 0.473 | 0.603 | 0.583 |
| $-W$ | 526.818 | 526.679 | 526.795 | 529.31 |

Table 2: Ionization potentials and total energy in the atomic unit ($e^2/a_0 = 1$) for the normal configuration of neutral Ar, obtained by various methods: HF, HFS, HFS'. Taken from "Atomic Structure," by E. U. Condon and Halis Odabasi, Cambridge University Press, 1980.

| Atom | HFS' | HFS | HF | Observed |
|------|---------|---------|---------|----------|
| He | -2.72 | -2.70 | -2.86 | -2.90 |
| Li | -7.17 | -7.15 | -7.43 | -7.48 |
| Ne | -127.49 | -127.38 | -128.55 | -128.94 |
| Ar | -524.51 | -524.35 | -526.82 | -527.60 |

Table 3: Total energies of atoms in the atomic unit ($e^2/a_0 = 1$). Taken from "Density-Functional Theory of Atoms and Molecules", by Robert G. Parr and Weitao Yang, Oxford University Press, 1989.

Clearly, this is not the total energy of the atom, because it counts the inter-electron Coulomb potential *twice*. However, when one *removes* an electron of an atom, you definitely want to include the interaction of that particular electron with every other electron in the atom. Namely, $-\lambda_i$ has the interpretation of the ionization energy to take an electron in the single-particle state $|\psi_i\rangle$ out of the atom. This interpretation is based on the assumption that the removal of the particular electron will not change the quantum states of other electrons significantly. Nonetheless, the interpretation allows the test of Hartree–Fock calculations by data.

Figs. 10,11 compare the HFS calculations of the ionization energies to the data, which show an overall agreement at a few percent level.

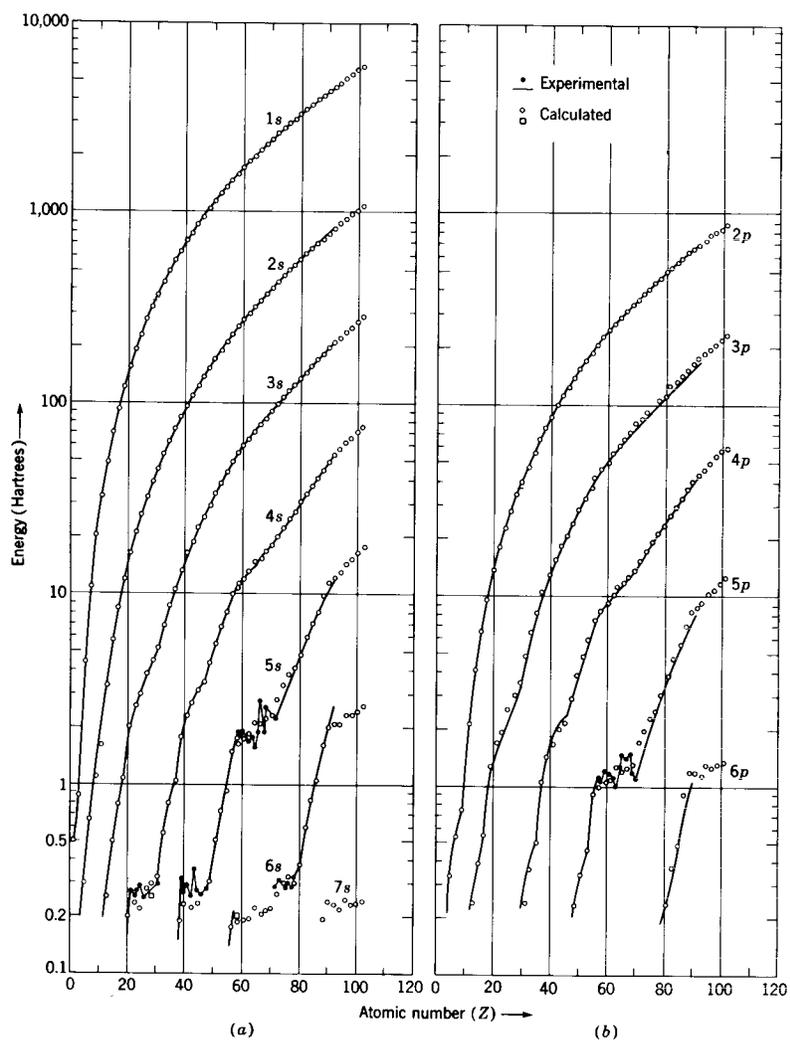


Figure 10: Comparison of ionization energies calculated with Hartree-Fock-Slater model to the data. Taken from "Quantum Theory of Matter," by John C. Slater, McGraw-Hill, 1968.

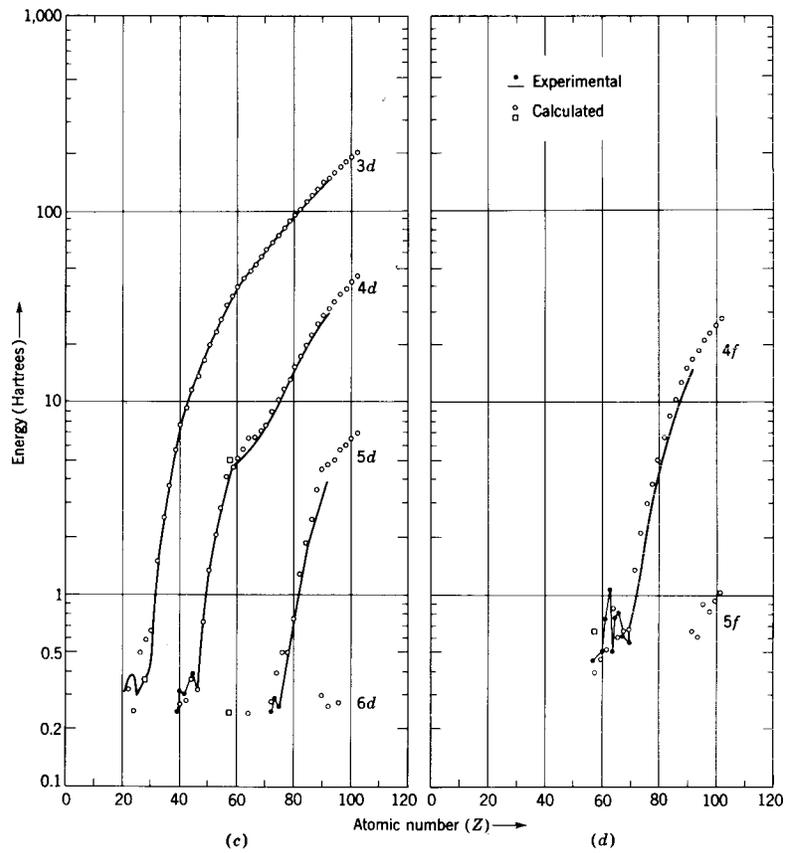


Fig. 7-2. Energy levels of the electrons, from Herman and Skillman's calculations (*op. cit.*), compared with experimental values.

Figure 11: Comparison of ionization energies calculated with Hartree–Fock–Slater model to the data. Taken from “Quantum Theory of Matter,” by John C. Slater, McGraw-Hill, 1968.

| Atom | HF | Observed |
|------|------|----------|
| Li | 5.3 | 5.4 |
| Be | 8.0 | 9.3 |
| B | 7.9 | 8.3 |
| C | 10.8 | 11.3 |
| N | 14.0 | 14.5 |
| O | 11.9 | 13.6 |
| F | 16.2 | 17.4 |
| Ne | 19.8 | 21.6 |
| Na | 4.9 | 5.1 |
| Ar | 14.8 | 15.8 |
| K | 4.0 | 4.3 |

Table 4: Ionization Potentials in electron volts of Some Light Atoms. Taken from “Density-Functional Theory of Atoms and Molecules”, by Robert G. Parr and Weitao Yang, Oxford University Press, 1989.

5 *LS* Coupling

For a given electronic configuration, there is still arbitrariness in how electrons occupy specific states. The empirical Hund’s rule states that the ground state is obtained by the following rule:

1. Maximize total spin S .
2. Then minimize L .
3. If an orbital is less than half-filled, $J = |L - S|$. If more than half-filled, $J = |L + S|$. (If it is exactly half-filled, $L = 0$ and $J = S$.)

In fact, all atoms except for Ce have the ground state consistent with the rule.

5.1 Less Than Half-Filled

To understand why the Hund’s rule holds, let us consider the electronic configuration $(np)^2$ for the group IV elements: C, Si, Ge, Sn, Pb. We assume that the rest of the electrons form a closed shell and do not consider the impact of remaining two electrons on them.

Each electron has $l = 1$, $s = 1/2$. We ignore the spin-orbit interaction, and hence total L and S are separately conserved. Therefore, we add two $l = 1$ to form $L = 0, 1, 2$ combinations, and two $s = 1/2$ to $S = 0, 1$. Note that $L = 0, 2$ and $S = 1$ are symmetric, while $L = 1$ and $S = 0$ anti-symmetric. Because the overall wave function must be anti-symmetric under the interchange of two electrons, the only allowed combinations are $L = 0, 2$ with $S = 0$ or $L = 1$ with $S = 1$. In the former case, the total angular momentum is $J = L$, and hence we find 1S_0 and 1D_2 states. Here, the spectroscopic symbols have the notation $^{2S+1}L_J$. For the latter case, we add $L = 1$ and $S = 1$ to obtain $J = 0, 1, 2$, and hence there are 3P_0 , 3P_1 , and 3P_2 states.

The orbital wave function of two electrons is given by

$$\psi(\vec{x}_1, \vec{x}_2) = R_{nl}(r_1)R_{nl}(r_2) \sum_{m_1, m_2} Y_l^{m_1}(\Omega_1)Y_l^{m_2}(\Omega_2)\langle llm_1m_2|LM\rangle. \quad (80)$$

In our case, $l = 1$, but I keep it general in the expressions. Note that the Clebsch–Gordan coefficients are symmetric or anti-symmetric when two l are the same,

$$\langle llm_2m_1|LM\rangle = (-1)^L\langle llm_1m_2|LM\rangle. \quad (81)$$

Therefore, the sum over m_1 and m_2 (subject to the constraint $m_1 + m_2 = M$) takes care of the symmetrization or anti-symmetrization automatically.

Now we calculate the expectation value of the Coulomb repulsion between two electrons. We use the multipole expansion of the Coulomb potential Eqs. (18,19) again. We also use the identity (Sakurai Eq. (3.7.73)),

$$\int d\Omega Y_l^{m*} Y_{l_1}^{m_1} Y_{l_2}^{m_2} = \sqrt{\frac{(2l_1 + 1)(2l_2 + 1)}{4\pi(2l + 1)}} \langle l_1 l_2 00 | l 0 \rangle \langle l_1 l_2 m_1 m_2 | l m \rangle \quad (82)$$

The expectation value is found to be

$$\begin{aligned} \langle LM | \frac{e^2}{r_{12}} | LM \rangle &= \sum_{\lambda} F^{\lambda}(np, np) \\ &\sum_{\substack{\mu, m_1, m_2 \\ m'_1, m'_2}} \langle llm_1m_2|LM\rangle \langle llm'_1m'_2|LM\rangle \langle l\lambda 00 | l 0 \rangle^2 \langle l\lambda m'_1\mu | lm_1 \rangle \langle l\lambda m_2\mu | lm'_2 \rangle, \end{aligned} \quad (83)$$

where

$$F^{\lambda}(np, np) = e^2 \int_0^{\infty} r_1^2 dr_1 r_2^2 dr_2 \frac{r_1^{\lambda}}{r_1^{\lambda+1}} R_{nl}(r_1)^2 R_{nl}(r_2)^2 > 0. \quad (84)$$

The variables λ, μ are “ l ” and “ m ” in the multipole expansion of the Coulomb potential. Because of the spherical symmetry of the problem, the result actually does not depend on M , even though it is not easy to see in this form. Due to the factor $\langle l\lambda 00|l0\rangle$, the sum over λ reduces to only $\lambda = 0$ and $\lambda = 2$ terms.

Wigner invented more compact notation called $3j$ - and $6j$ -symbols. The result can be rewritten as

$$\langle LM|\frac{e^2}{r_{12}}|LM\rangle = \sum_{\lambda} F^{\lambda}(np, np)(-1)^L(2l+1)^2 \begin{pmatrix} l & l & \lambda \\ 0 & 0 & 0 \end{pmatrix} \left\{ \begin{matrix} l & l & L \\ l & l & \lambda \end{matrix} \right\}. \quad (85)$$

The symbol with the parenthesis is the $3j$ -symbol, while that with the curly braces is the $6j$ -symbol. You can find their definitions in many quantum mechanics textbooks, such as Messiah. Mathematica has both $3j$ - and $6j$ -symbols built in, and their evaluations are very easy. This expression also makes it clear that the result does not depend on M .

In our case of $l = 1$, we find

$$\langle (np)^2, L = 0|\frac{e^2}{r_{12}}|(np)^2, L = 0\rangle = F^0 + \frac{2}{5}F^2, \quad (86)$$

$$\langle (np)^2, L = 1|\frac{e^2}{r_{12}}|(np)^2, L = 1\rangle = F^0 - \frac{1}{5}F^2, \quad (87)$$

$$\langle (np)^2, L = 2|\frac{e^2}{r_{12}}|(np)^2, L = 2\rangle = F^0 + \frac{1}{25}F^2. \quad (88)$$

Therefore, $L = 1$ state has the lowest energy. This can be understood intuitively in the following fashion. When the spatial wave function is anti-symmetrized, the probability for two electrons to come close is minimized, and so is the Coulomb repulsion energy.

Since the anti-symmetric orbital wave function minimizes the Coulomb repulsion, it necessarily picks symmetric spin wave function. In our case, 3P_J states have lower energies than 1S_0 and 1D_2 states. It is important to note that $S = 1$ (maximum total spin) is chosen not because there is an interaction that prefers to line up the spins, but rather because the Coulomb repulsion prefers the orbital wave function to be as anti-symmetric as possible, and hence the spin wave function as symmetric as possible due to the overall anti-symmetry of the multi-fermion wave functions. This is the origin of the magnetism; spins want to line up due to the Fermi statistics. Now we understand the rules 1. and 2.

The last rule is the consequence of the spin-orbit coupling. As we have seen in the case of hydrogen-like atoms, the spin-orbit coupling Eq. (6) prefers

| | |
|----|------|
| C | 1.13 |
| Si | 1.48 |
| Ge | 1.50 |
| Sn | 1.39 |
| Pb | 1.62 |

Table 5: The ratio of energy splittings in group IV elements defined in Eq. (89), to be compared to 1.5 we calculated.

the spin and the orbital angular momentum to be anti-aligned. This carries over to the multi-electron configuration as well. Hence, the rule 3. In our case of $(np)^2$ configurations, the states are ordered 3P_0 , 3P_1 , and 3P_2 from the ground state to the excited states. In general, by anti-aligning L and S , we find $J = |L - S|$.

Putting everything together, we find the $(np)^2$ states are ordered as 3P_0 , 3P_1 , 3P_2 , 1D_2 , 1S_0 from below. Indeed, the spectrum data at NIST web site <http://physics.nist.gov/PhysRefData/Handbook/periodictable.htm> confirms this result for the group IV elements.

We can perform quantitative tests of the result. The energy splittings are given by

$$\frac{E({}^1S) - E({}^1D)}{E({}^1D) - E({}^3P)} = \frac{3}{2}. \quad (89)$$

To use the data, we need to eliminate the energy splitting due to the spin-orbit coupling, which can be done by calculating the weighted average of the energies

$$E({}^3P) = \frac{1}{9}(E({}^3P_0) + 3E({}^3P_1) + 5E({}^3P_2)). \quad (90)$$

Using the data at NIST, we find numbers in Table 5.

The agreement is excellent for medium-sized atoms, Si and Ge. The worse result for the heavier atoms is due to the fact that the spin-orbit interaction is more important for them. Because the spin-orbit coupling is a relativistic effect, it is proportional to $(v/c)^2 \simeq (Z\alpha)^2$ and hence grows with Z . In general, the LS coupling scheme does not work very well. An alternative scheme called jj coupling may be used, where l and s are summed for individual electron first, and then each j is combined together to form the total J . It is known that neither LS and jj couplings provide good results for large atoms; *i.e.*, Z is not very small, but not very large either. Quantitative understanding of the spin-orbit coupling is somewhat complicated,

| level | data | MCHF |
|-----------|----------|----------|
| 3P_0 | 0 | 0 |
| 3P_1 | 16.41671 | 16.33 |
| 3P_2 | 43.41350 | 43.03 |
| 1D_2 | 10192.66 | 10268.23 |
| 1S_2 | 21648.02 | 21818.60 |

Table 6: The comparison of carbon atomic levels with the MCHF calculations. Taken from <http://atoms.vuse.vanderbilt.edu/> The unit is cm^{-1} .

because there are spin-orbit couplings associated with both nucleus-electron and electron-electron Coulomb potentials. In practice, the nucleus-electron spin-orbit coupling is more important than the electron-electron one, but the detailed calculation requires both.

You may be surprised that the agreement is bad for the smallest atom, C. This can be understood in the following way. In the carbon atom, the “closed shell” we ignored in our discussion consists of four electrons, while we studied the remaining two electrons. Because the number of electrons in the “closed shell” and in the “open shell” are comparable, the Coulomb repulsion of the valence electrons affect the wave functions of the “closed shell” electrons. Strictly speaking, this is an effect at the second-order in perturbation, yet it seems to be quite significant.

The professionals in the theoretical atomic physics use the Hartree–Fock method to calculate the wave functions, and form their linear combinations to obtain specific ${}^{2S+1}L_J$ states. This method is called the Multi-Configuration Hartree–Fock. The comparison of data and calculations is shown in Table 6 for the carbon atom; the agreement is impressive.

5.2 Half-Filled

When an orbital is half-filled, namely when $(2l + 1)$ electrons occupy an nl orbital, the maximum spin is $S = l + \frac{1}{2}$, while the totally anti-symmetric orbital wave function gives $L = 0$. The orbital wave function is nothing by the Slater determinant of all m states from $m = -l$ to $m = l$. There is only one such wave function, and hence the total orbital angular momentum is $L = 0$ (multiplicity one). Because $L = 0$, the only possible total angular momentum is $J = S = l + \frac{1}{2}$, and hence the rule 3. is not needed.

| | |
|----|---------|
| O | 1.14 |
| S | 1.43 |
| Se | 1.49 |
| Te | 1.49 |
| Po | no data |

Table 7: The ratio of energy splittings of group VI elements defined in Eq. (89), to be compared to 1.5 we calculated.

5.3 More Than Half-Filled

When an orbital is more than half-filled, it becomes awkward to discuss each electron. There is no way to totally anti-symmetrize the orbital wave function because each m is already used; some of the same orbital wave function needs to be used twice. Correspondingly, the spin wave function should not be totally symmetric. Both the orbital and spin wave functions are partially anti-symmetric and partially symmetric, so that their produce is totally anti-symmetric. Such a “mixed-symmetry” wave functions are not easy to discuss on general grounds.

However, there is a useful trick to discuss electrons in an orbital that is more than half-filled. It uses the concept of “holes.” For example, consider the $(np)^4$ configuration (group VI elements). The orbital accommodates six electrons, while only four are there. If all six states are filled, we know that the overall Slater determinant has $L = S = J = 0$. Therefore, instead of considering four electrons in the np orbital, we can consider removing two electrons from the filled np orbital, or two “holes” in the np orbital.

A hole means a vacancy. Therefore, a hole carries a positive electric charge relative to the filled state. Concerning the Coulomb repulsion, the calculation of the expectation value is exactly the same as that for the electrons because $(-e)^2 = e^2$. Therefore, the previous result can be used without modification on the 3P , 1D , and 1S states.

The energy splittings in the group VI elements are shown in Table 7. Again there is an excellent agreement for the medium-sized atoms, while the agreement is bad for the smallest one, O. (There does not seem data for Po.)

Therefore the rules 1. and 2. are understood precisely the same way as for the case of less than half-filled orbitals. Namely, the energy is the lowest when the orbital wave function is totally anti-symmetrized for *holes*, which requires the totally symmetrized spin wave function for *holes*.

| level | data | MCHF |
|---------|-----------|----------|
| 3P_2 | 0 | 0 |
| 3P_1 | 158.265 | 156.05 |
| 3P_0 | 226.977 | 223.33 |
| 1D_2 | 15867.862 | 15868.34 |
| 1S_2 | 33792.583 | 33792.22 |

Table 8: The comparison of oxygen atomic levels with the MCHF calculations. Taken from <http://atoms.vuse.vanderbilt.edu/> The unit is cm^{-1} .

The rule 3., however, appears different from the case of less than half-filled orbitals. This is also understood using the concept of hole. Because the hole has the opposite electric charge from that of the electron, the sign of the spin-orbit coupling of the electron-nucleus Coulomb potential reverses. Therefore a hole prefers to have its spin and orbital angular momenta *aligned*, instead of anti-aligned. Indeed, the data show that the states are ordered as 3P_2 , 3P_1 , 3P_0 , 1D_2 , 1S_0 from below. In Table 8, the data and the MCHF calculations are compared. The agreement is again excellent.