

# 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,  $\text{He}^+$ ,  $\text{Li}^{++}$ ,  $\text{Be}^{3+}$ , 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  $a = \hbar^2/m_e^2$  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,  $a = a_B/Z$ .

## 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

$$H = \sum_i \left( \frac{\vec{p}_i^2}{2m} - \frac{Ze^2}{r_i} \right) + \sum_{i < j} \frac{e^2}{r_{ij}}. \quad (5)$$

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.

We regard the single particle Hamiltonian

$$H_0 = \sum_i \left( \frac{\vec{p}_i^2}{2m} - \frac{Ze^2}{r_i} \right) \quad (6)$$

as the unperturbed and the Coulomb repulsion terms

$$\Delta H = \sum_{i < j} \frac{e^2}{r_{ij}} \quad (7)$$

as perturbation to the system.

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

$$|1s^2\rangle = \frac{1}{\sqrt{2}} [|1s^\uparrow 1s^\downarrow\rangle - |1s^\downarrow 1s^\uparrow\rangle]. \quad (8)$$

The unperturbed Hamiltonian has an eigenvalue on this state

$$H_0|1s^2\rangle = E_0|1s^2\rangle = 2 \left( -\frac{Z^2e^2}{2a_B} \right) |1s^2\rangle. \quad (9)$$

This binding energy is too big compared to experimental values (see Table 1. **If you happen to know the data on  $\text{H}^-$  binding energy, let me know!**

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

$$\Delta E = \langle 1s^2 | \frac{e^2}{r_{12}} | 1s^2 \rangle. \quad (10)$$

Using the unperturbed wave function Eq. (8), we find

$$\begin{aligned} \Delta E = \frac{1}{2} & \left[ \langle 1s^\uparrow 1s^\downarrow | \frac{e^2}{r_{12}} | 1s^\uparrow 1s^\downarrow \rangle - \langle 1s^\uparrow 1s^\downarrow | \frac{e^2}{r_{12}} | 1s^\downarrow 1s^\uparrow \rangle \right. \\ & \left. - \langle 1s^\downarrow 1s^\uparrow | \frac{e^2}{r_{12}} | 1s^\uparrow 1s^\downarrow \rangle + \langle 1s^\downarrow 1s^\uparrow | \frac{e^2}{r_{12}} | 1s^\downarrow 1s^\uparrow \rangle \right]. \quad (11) \end{aligned}$$

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

Table 1: Binding energies as measured  $E_{\text{exp}}$ ,  $E_0$  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  $E_{\text{var}}$  for two-electron atoms. The numbers are from “Introduction to Quantum Mechanics,” Linus Pauling and E. Bright Wilson, Jr., McGraw-Hill, 1935.

However, because  $\Delta H$  commutes with the spin, the expression simplifies to

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

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

$$\Delta E = \langle 1s1s | \frac{e^2}{r_{12}} | 1s1s \rangle. \quad (13)$$

This is calculated by the integral

$$\Delta E = \frac{Z^6}{a_B^6} \int d\vec{x}_1 d\vec{x}_2 \frac{e^2}{r_{12}} (2e^{-Zr_1/a_B} Y_0^0(\theta_1, \phi_1))^2 (2e^{-Zr_2/a_B} Y_0^0(\theta_2, \phi_2))^2. \quad (14)$$

Because  $Y_0^0 = 1/\sqrt{4\pi}$  and the only piece that depends on angles is  $r_{12} = \sqrt{r_1^2 + r_2^2 - 2r_1r_2 \cos \theta_{12}}$ , 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

$$\frac{1}{r_{12}} = \sum_{l=0}^{\infty} \frac{r_{<}^l}{r_{>}^{l+1}} P_l(\cos \theta_{12}), \quad (15)$$

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

$$P_l(\cos \theta_{12}) = \frac{4\pi}{2l+1} \sum_{m=-l}^l Y_l^{m*}(\theta_1, \phi_1) Y_l^m(\theta_2, \phi_2). \quad (16)$$

Going back to Eq. (14), and replacing  $e^2/r_{12}$  using the identities Eq. (15,16), angular integrals in  $\vec{x}_1, \vec{x}_2$  selects only  $l = 0, m = 0$  piece in the summation. Therefore one finds

$$\Delta E = \frac{Z^6}{a_B^6} \int_0^\infty r_1^2 dr_1 r_2^2 dr_2 16 \frac{e^2}{r_{>}} e^{-2Z(r_1+r_2)} = \frac{5}{8} \frac{Z e^2}{a_B}. \quad (17)$$

Adding this energy to the single-particle energy Eq. (9), 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

$$\psi_{1s}(\vec{x}) = \left( \frac{Z'}{a_B} \right)^{3/2} e^{-Z'r/a_B}. \quad (18)$$

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  $\psi_{1s}$  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

$$\langle 1s | \frac{\vec{p}^2}{2m} - \frac{Z e^2}{r} | 1s \rangle = \frac{Z' e^2}{2a_B} - \frac{Z Z' e^2}{a_B}. \quad (19)$$

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

$$\langle 1s 1s | \frac{e^2}{r_{12}} | 1s 1s \rangle = \frac{5}{8} \frac{Z' e^2}{a_B}. \quad (20)$$

Therefore,

$$\langle 1s^2 | H | 1s^2 \rangle = \frac{e^2}{a_B} \left[ 2 \left( \frac{Z'^2}{2} - Z Z' \right) + \frac{5}{8} Z' \right]. \quad (21)$$

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

$$E_{\text{var}} = -\frac{e^2}{a_B} \frac{(16Z - 5)^2}{256}. \quad (22)$$

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. (5) 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. (5), 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  $\Delta H$  using the following decomposition:

$$E_0 = \sum_i E_{\lambda_i}, \quad (23)$$

$$\Delta E = \sum_{i < j} \left[ \langle \lambda_i \lambda_j | \frac{e^2}{r_{ij}} | \lambda_i \lambda_j \rangle - \langle \lambda_i \lambda_j | \frac{e^2}{r_{ij}} | \lambda_j \lambda_i \rangle \right]. \quad (24)$$

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 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,  $\text{Be}^+$ ,  $\text{B}^{++}$ , 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 where people didn't consider  $l = 0$  state because of the classical prejudice.) 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 neutral atoms,

$$Z = 4\pi \int \rho(r)r^2 dr. \quad (25)$$

The distribution of electron determines the Coulomb potential  $\phi$  according to the Poisson equation

$$\Delta\phi = \frac{1}{r} \frac{d^2}{dr^2} r\phi = 4\pi e\rho(r) - 4\pi Ze\delta(\vec{x}). \quad (26)$$

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

$$\frac{1}{r} \frac{d^2}{dr^2} r\phi = 4\pi e\rho(r) \quad (27)$$

and impose the boundary condition

$$\lim_{r \rightarrow 0} r\phi(r) = Ne \quad (28)$$

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  $N = Z$ . Then the potential energy for an electron is given by

$$V(r) = -e\phi(r). \quad (29)$$

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  $\varepsilon_F$  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

$$n(\vec{r}, \vec{p}) = \begin{cases} \frac{2}{(2\pi\hbar)^3} & \text{for } \frac{\vec{p}^2}{2m} - e\phi < \varepsilon_F \\ 0 & \text{for } \frac{\vec{p}^2}{2m} - e\phi > \varepsilon_F \end{cases} \quad (30)$$

From this point on, we define  $\Phi$  by

$$e\Phi = e\phi + \varepsilon_F \quad (31)$$

so that the number density is written as

$$n(\vec{r}, \vec{p}) = \begin{cases} \frac{2}{(2\pi\hbar)^3} & \text{for } \frac{\vec{p}^2}{2m} - e\Phi < 0 \\ 0 & \text{for } \frac{\vec{p}^2}{2m} - e\Phi > 0 \end{cases} \quad (32)$$

$\Phi$  still satisfies the same Poisson equation Eq. (26) because a constant disappears under the Laplacian  $\Delta$  and the same boundary condition Eq. (28).

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. (32), the phase space density is constant  $2/(2\pi\hbar)^3$  up to  $p = (2me\Phi)^{1/2}$  and hence

$$\rho(r) = \begin{cases} \frac{2}{(2\pi\hbar)^3} \frac{4\pi}{3} (2me\Phi)^{3/2} & (x > 0) \\ 0 & (x < 0) \end{cases} . \quad (33)$$

Therefore we now try to solve coupled equations Eq. (26) and Eq. (33) under the boundary condition Eq. (28). This is done in a  $Z$ -independent way by introducing variable  $x$  by

$$r = Z^{-1/3}bx, \quad b = \frac{1}{2} \left( \frac{3\pi}{4} \right)^{2/3} \frac{\hbar^2}{me^2} \simeq 0.5 \text{ \AA}, \quad (34)$$

and a new function  $\chi$  defined by

$$\Phi(r) = \frac{Ze}{r} \chi(r). \quad (35)$$



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

$$\rho(r) = \begin{cases} \frac{Z^2}{4\pi b^3} \left(\frac{\chi}{x}\right)^{3/2} & (\chi > 0) \\ 0 & (\chi < 0) \end{cases}. \quad (36)$$

The Poisson equation Eq. (26) then reads as

$$\frac{d^2\chi}{dx^2} = \begin{cases} x^{-1/2}\chi^{3/2} & (\chi > 0) \\ 0 & (\chi < 0) \end{cases}. \quad (37)$$

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  $\chi''$  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. (36)), all electrons are inside the radius  $x_0$ . Therefore the total number of electrons is

$$\begin{aligned} N &= \int_0^{Z^{-1/3}bx_0} 4\pi r^2 dr \frac{Z^2}{4\pi b^3} \left(\frac{\chi}{x}\right)^{3/2} = Z \int_0^{x_0} dx x \chi(x)'' \\ &= Z[x\chi' - \chi]_0^{x_0} = Z[x_0\chi'(x_0) + 1]. \end{aligned} \quad (38)$$

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  $\chi'(0) = -1.588071$  to solve the differential equation numerically.

A technical remark. When you solve the differential equation Eq. (37) 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

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

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.

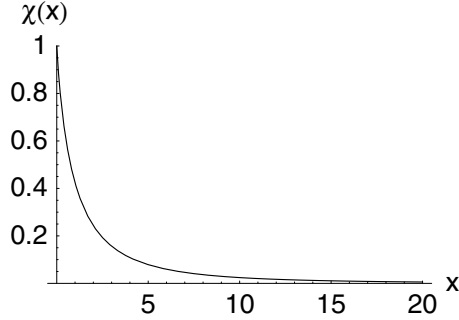


Figure 1: Numerical calculation of  $\chi(x)$  for neutral atoms.

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

$$\chi(x) = (x - x_0)\chi'(x_0) = -\frac{r - r_0}{r_0} \frac{Z - N}{Z}, \quad (39)$$

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

$$e\phi = e\Phi - \varepsilon_F = -\frac{Ze^2}{r} \frac{r - r_0}{r_0} \frac{Z - N}{Z} - \varepsilon_F = \frac{(Z - N)e^2}{r} - \frac{(Z - N)e^2}{r_0} - \varepsilon_F. \quad (40)$$

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

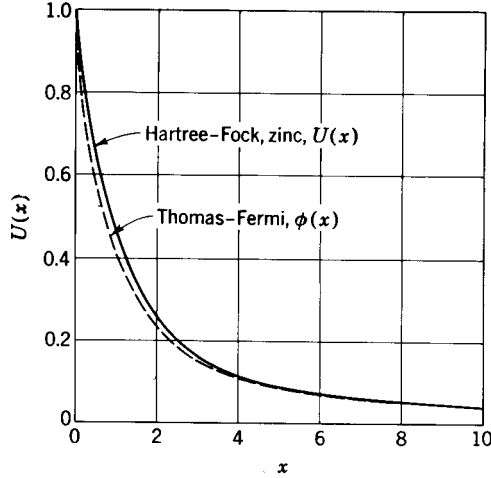
$$\varepsilon_F = -\frac{(Z - N)e}{r_0}. \quad (41)$$

The solution is obtained by  $\chi(x)$  with  $\chi'(x_0) < -1.588071$  so that  $x_0\chi'(0) = -(Z - N)/Z$ .

Thomas–Fermi model is a crude model based on semi-classical argument and statistical treatment, but is not so bad in practice. In Figs. 2,3,4, we will 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.

## 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



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

Figure 2: 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.

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.

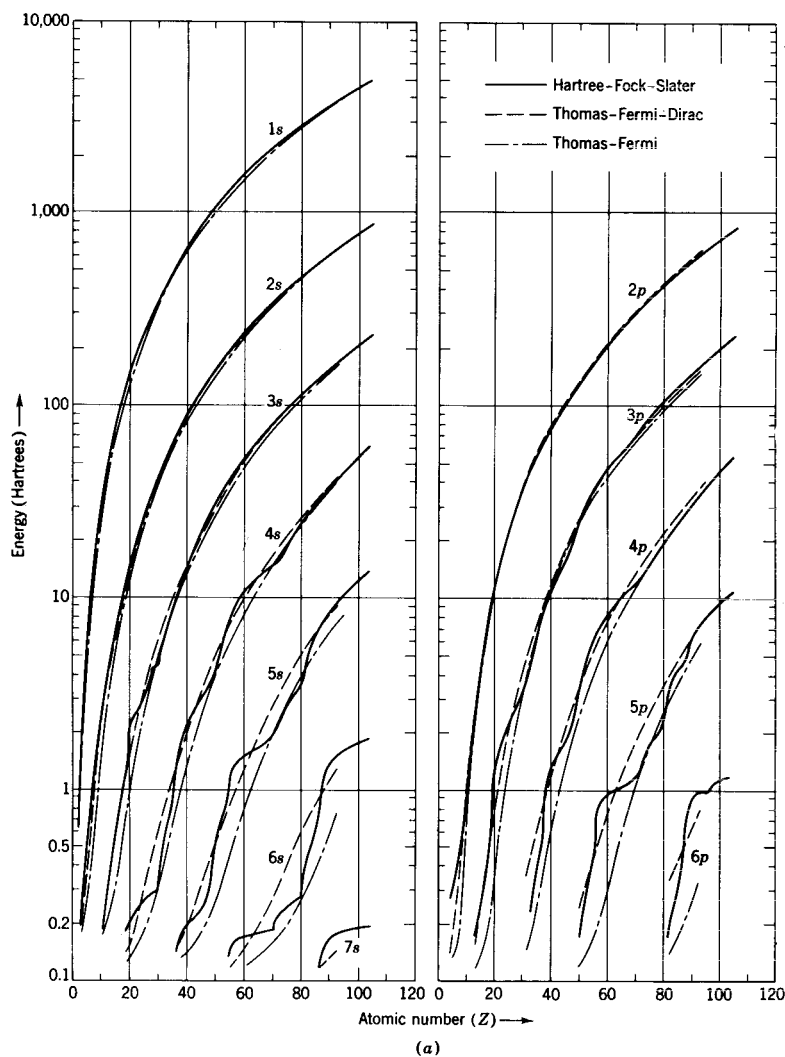
The basic idea is the self-consistency, as in the Thomas–Fermi model. The difference is that instead of using a smooth semi-classical electron number density  $\rho(r)$ , we study the single-particle wave functions.

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

$$|\Psi\rangle = \frac{1}{N!} \det \begin{pmatrix} |\psi_1(1)\rangle & |\psi_1(2)\rangle & \cdots & |\psi_1(N)\rangle \\ |\psi_2(1)\rangle & |\psi_2(2)\rangle & \cdots & |\psi_2(N)\rangle \\ \vdots & \vdots & \ddots & \vdots \\ |\psi_N(1)\rangle & |\psi_N(2)\rangle & \cdots & |\psi_N(N)\rangle \end{pmatrix}. \quad (42)$$

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. (5), and the expectation value of the Hamiltonian is given by

$$\begin{aligned} E &= \langle \Psi | H | \Psi \rangle \\ &= \sum_i \langle \psi_i | \left( \frac{\vec{p}^2}{2m} - \frac{Ze^2}{r} \right) | \psi_i \rangle \end{aligned}$$



**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 3: 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.

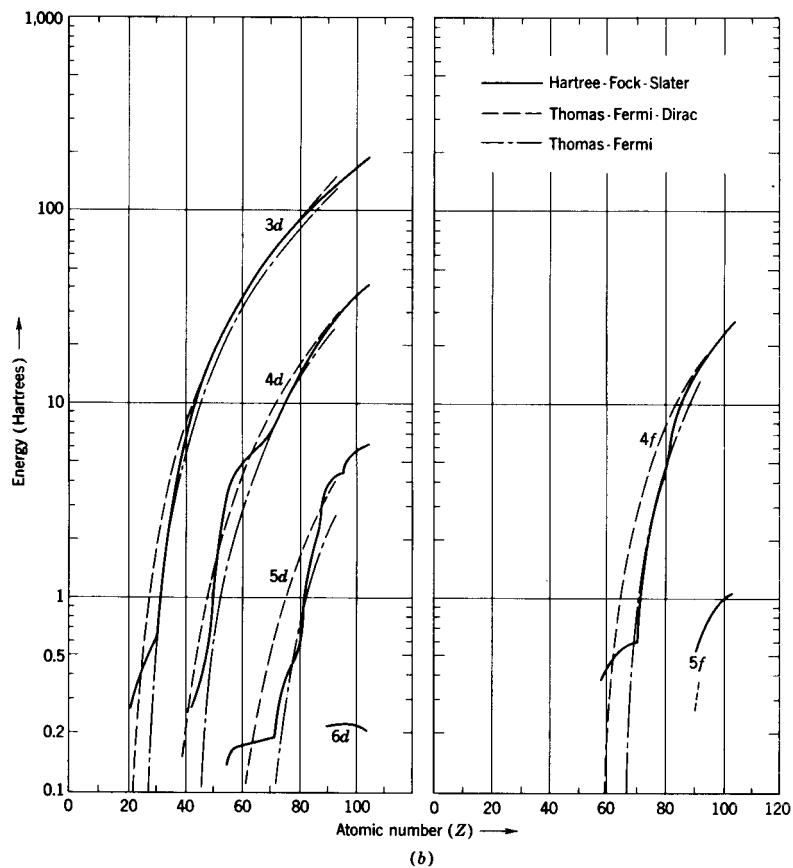


Fig. 16-3.

Figure 4: 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.

$$+ \sum_{i < j} \left[ \langle \psi_i(1)\psi_j(2) | \frac{e^2}{r_{12}} | \psi_i(1)\psi_j(2) \rangle - \langle \psi_i(1)\psi_j(2) | \frac{e^2}{r_{12}} | \psi_j(1)\psi_i(2) \rangle \right]. \quad (43)$$

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  $\langle\psi_i|$ ,

$$\begin{aligned} \delta E &= (\delta\langle\psi_i|) \left( \frac{\vec{p}^2}{2m} - \frac{Ze^2}{r} \right) |\psi_i\rangle \\ &+ \sum_{j \neq i} (\delta\langle\psi_i(1)|) \left[ \langle\psi_j(2) | \frac{e^2}{r_{12}} | \psi_i(1)\psi_j(2) \rangle - \langle\psi_j(2) | \frac{e^2}{r_{12}} | \psi_j(1)\psi_i(2) \rangle \right]. \end{aligned} \quad (44)$$

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

$$\delta[E - \lambda_{ij}(\langle\psi_i|\psi_j\rangle - \delta_{ij})] = 0, \quad (45)$$

where  $\lambda_{ij}$  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

$$\begin{aligned} &\left( \frac{\vec{p}^2}{2m} - \frac{Ze^2}{r} \right) |\psi_i\rangle \\ &+ \sum_{j \neq i} \left[ \langle\psi_j(2) | \frac{e^2}{r_{12}} | \psi_i(1)\psi_j(2) \rangle - \langle\psi_j(2) | \frac{e^2}{r_{12}} | \psi_j(1)\psi_i(2) \rangle \right] - \lambda_{ij} |\psi_j\rangle = 0. \end{aligned} \quad (46)$$

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

$$\left( -\frac{\hbar^2 \Delta}{2m} - \frac{Ze^2}{r} \right) \psi_i(\vec{x})$$

$$\begin{aligned}
& + \sum_{j \neq i} \int d\vec{y} \psi_j(\vec{y})^* \left[ \frac{e^2}{|\vec{x} - \vec{y}|} \psi_j(\vec{y}) \psi_i(\vec{x}) - \frac{e^2}{|\vec{x} - \vec{y}|} \psi_i(\vec{y}) \psi_j(\vec{x}) \delta_{m_{si}, m_{sj}} \right] \\
& = \lambda_{ij} \psi_j(\vec{x}).
\end{aligned} \tag{47}$$

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  $\lambda_{ij}$  form a hermitean matrix, and we can always go to the basis of single particle states where the matrix  $\lambda_{ij}$  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. (47) 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  $\psi_i$ , but this trick makes the equation the same for all  $i$ ,

$$\left( -\frac{\hbar^2 \Delta}{2m} - \frac{Ze^2}{r} \right) \psi_i(\vec{x}) + V_{ee}(\vec{x}) \psi_i(\vec{x}) - \int d\vec{y} V_{ee}^{ex}(\vec{x}, \vec{y}) \psi_i(\vec{y}) = \lambda_i \psi_i(\vec{x}), \tag{48}$$

with

$$V_{ee}(\vec{x}) = \int d\vec{y} \frac{e^2}{|\vec{x} - \vec{y}|} \sum_j |\psi_j(\vec{y})|^2 \tag{49}$$

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

$$V_{ee}^{ex} = \sum_j \frac{e^2}{|\vec{x} - \vec{y}|} \psi_j^*(\vec{y}) \psi_j(\vec{x}) \delta_{m_{si}, m_{sj}} \tag{50}$$

is the exchange term. Eq. (48) 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

$$V_C(\vec{x}) = -\frac{Ze^2}{r} + \int d\vec{y} \frac{e^2}{|\vec{x} - \vec{y}|} \rho(\vec{y}) \tag{51}$$

for every state  $\psi_i(\vec{x})$ , where  $V_{ee}$  is determined by  $\psi_i(\vec{x})$  as in Eq. (49) 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. (48), 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

$$\psi_i(\vec{x}) = \frac{1}{\sqrt{V}} e^{i\vec{k}_i \cdot \vec{x}}, \quad (52)$$

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

$$\int d\vec{y} \psi_j(\vec{y})^* \frac{e^2}{|\vec{x} - \vec{y}|} \psi_j(\vec{x}) \psi_i(\vec{y}) = \frac{1}{V} \frac{4\pi e^2}{|\vec{k}_i - \vec{k}_j|^2} \psi_i(\vec{x}). \quad (53)$$

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

$$\rho = \frac{N}{V} = \frac{2}{(2\pi)^3} \frac{4\pi}{3} k_F^3. \quad (54)$$

Going back to Eq. (53) and performing the integral,

$$\begin{aligned} & \sum_j \int d\vec{y} \psi_j(\vec{y})^* \frac{e^2}{|\vec{x} - \vec{y}|} \psi_j(\vec{x}) \psi_i(\vec{y}) \delta_{m_{s_i}, m_{s_j}} \\ &= \frac{1}{(2\pi)^3} V \int_0^{k_F} d\vec{k}_j \frac{1}{V} \frac{4\pi e^2}{|\vec{k}_i - \vec{k}_j|^2} \psi_j(\vec{x}) = e^2 \frac{k_F}{2\pi} 4F(\eta) \psi_j(\vec{x}), \end{aligned} \quad (55)$$



where

$$F(\eta) = \frac{1}{2} + \frac{1 - \eta^2}{4\eta} \ln \frac{1 + \eta}{1 - \eta} \quad (56)$$

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. (51) must be correspondingly corrected to

$$V_C(\vec{x}) = -\frac{Ze^2}{r} + \int d\vec{y} \frac{e^2}{|\vec{x} - \vec{y}|} \rho(\vec{y}) - e^2 \left( \frac{3}{8\pi} \rho(\vec{x}) \right)^{1/3} 4F(\eta). \quad (57)$$

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

$$F(\eta)_{\text{average}} = \frac{\int_0^1 \eta^2 F(\eta) d\eta}{\int_0^1 \eta^2 d\eta} = \frac{3}{4} \quad (58)$$

and we find

$$V_C(\vec{x}) = -\frac{Ze^2}{r} + \int d\vec{y} \frac{e^2}{|\vec{x} - \vec{y}|} \rho(\vec{y}) - 3e^2 \left( \frac{3}{8\pi} \rho(\vec{x}) \right)^{1/3}. \quad (59)$$

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  $\lambda_i$ . Going back to Eq. (47) for diagonal  $\lambda_i$ , we take inner product with  $\langle \psi_i |$  and sum over  $i$ :

$$\begin{aligned} & \sum_i \langle \psi_i | \left( \frac{\vec{p}^2}{2m} - \frac{Ze^2}{r} \right) | \psi_i \rangle \\ & + \sum_{i,j} \left[ \langle \psi_i(1)\psi_j(2) | \frac{e^2}{r_{12}} | \psi_i(1)\psi_j(2) \rangle - \langle \psi_i(1)\psi_j(2) | \frac{e^2}{r_{12}} | \psi_j(1)\psi_i(2) \rangle \right] = \sum_i \lambda_i. \end{aligned} \quad (60)$$

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

	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.

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. 5,6 compare the HFS calculations of the ionization energies to the data, which show an overall agreement at a few percent level. **If any of you can find comparison of full HFS calculations to data in more recent books, let me know!**

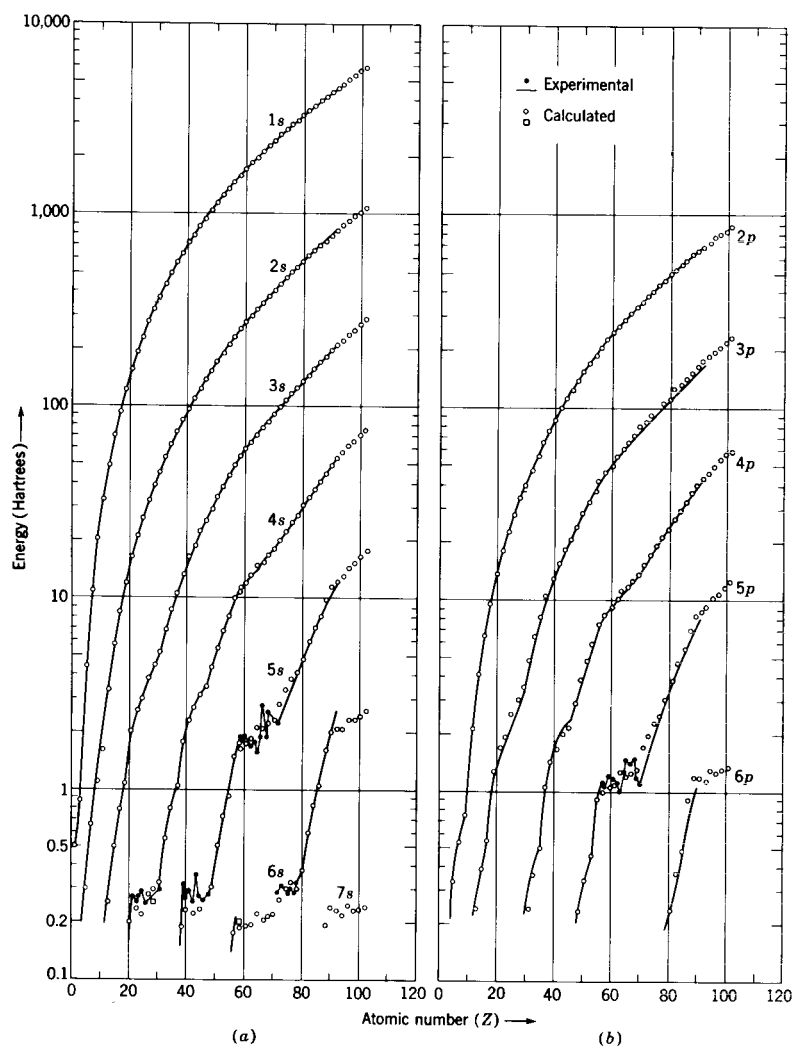
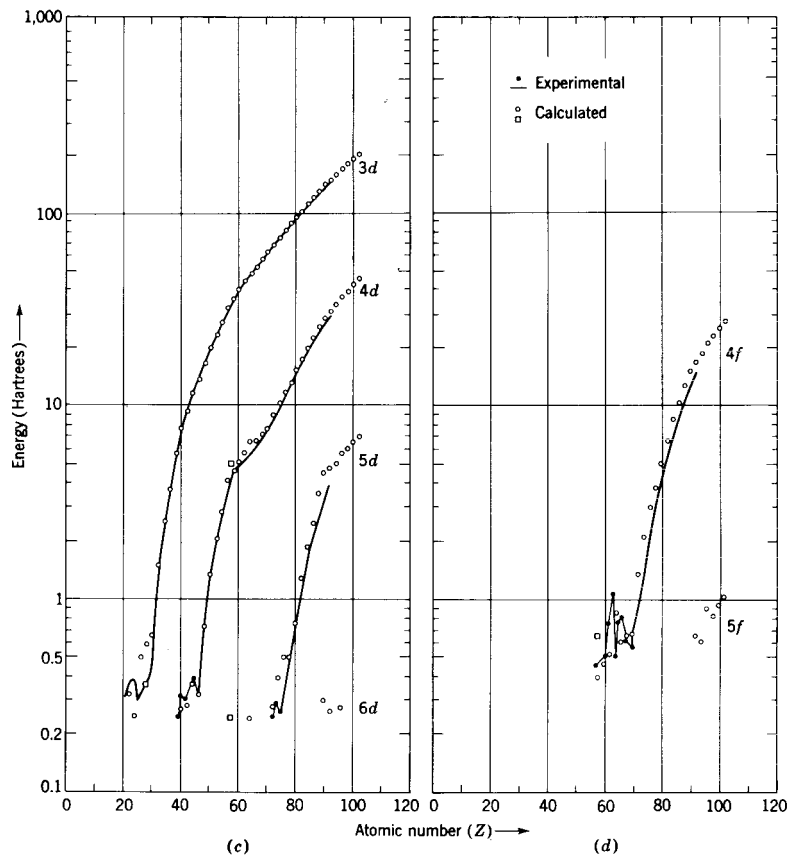


Figure 5: Comparison of ionization energies calculated with Hartree-Fock-Slater model to the data. Taken from "Quantum Theory of Matter," by John C. Slater, McGraw-Hill, 1968.



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

Figure 6: 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.