

3 / Self-consistent Field

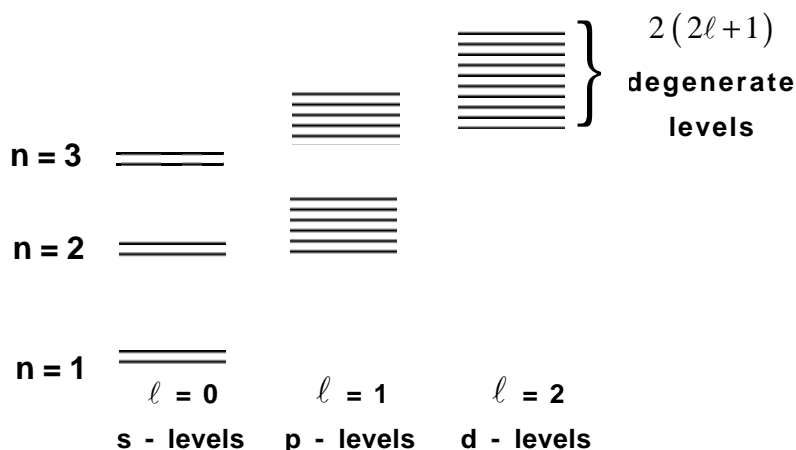
3.1. The self-consistent field (scf) procedure

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One of the first successes of quantum theory after the Hydrogen atom was to explain the periodic table of atoms by combining the energy levels obtained from the Schrodinger equation with the Pauli exclusion principle requiring that each level be occupied by no more than one electron. The energy eigenvalues of the Schrodinger equation for each value of ' ℓ ' starting from $\ell = 0$ (see Eq.(1.3.8)) are numbered with integer values of ' n ' starting from $n = \ell + 1$. For any (n, ℓ) there are $(2\ell + 1)$ levels with distinct angular wavefunctions (labeled with another index ' m ') all of which have the same energy. For each (n, ℓ, m) there is an up-spin and a down-spin level making the number of degenerate levels equal to $2(2\ell + 1)$ for a given (n, ℓ) . The energy levels look something like this



The elements of the periodic table are arranged in order as the number of electrons increase by one from one atom to the next, and their electronic structure can be written as Hydrogen: $1s^1$, Helium: $1s^2$, Lithium: $1s^2 2s^1$, Beryllium: $1s^2 2s^2$, Boron: $1s^2 2s^2 2p^1$ etc, where the superscript indicates the number of electrons occupying a particular orbital.

How do we calculate the energy levels for a multielectron atom? The time-independent Schrodinger equation

$$E_{\alpha} \Phi_{\alpha}(\vec{r}) = H_{\text{op}} \Phi_{\alpha}(\vec{r}) \quad \text{where} \quad H_{\text{op}} \equiv -\frac{\hbar^2}{2m} \nabla^2 + U(\vec{r})$$

provides a fairly accurate description of the observed spectra of all atoms, not just the Hydrogen atom. However, multielectron atoms involve electron-electron interactions which is included by adding a "self-consistent field (scf)", $U_{\text{scf}}(\vec{r})$, to the nuclear potential $U_{\text{nuc}}(\vec{r})$: $U(\vec{r}) = U_{\text{nuc}}(\vec{r}) + U_{\text{scf}}(\vec{r})$, just as in Section 1.4 we added an extra potential to the Laplace potential U_L (see Eq.(1.4.1b)). The nuclear potential U_{nuc} , like U_L , is fixed, while U_{scf} depends on the electronic wavefunctions and has to be calculated from a self-consistent iterative procedure. In this chapter we will describe this procedure and the associated conceptual issues.

3.1. The self-consistent field (SCF) procedure

Consider a Helium atom consisting of two electrons bound to a nucleus with two positive charges '+2q'. What will the energy levels look like? Our first guess would be simply to treat it just like a hydrogen atom except that the potential is

$$U(\vec{r}) = -2q^2 / 4\pi\epsilon_0 r \quad \text{instead of} \quad U(\vec{r}) = -q^2 / 4\pi\epsilon_0 r$$

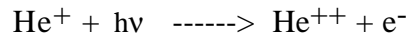
If we solve the Schrodinger equation with $U(\vec{r}) = -Zq^2 / 4\pi\epsilon_0 r$ we will obtain energy levels given by

$$E_n = -(Z^2 / n^2) E_0 = -54.4 \text{ eV} / n^2 \quad (Z = 2)$$

just as predicted by the simple Bohr model (see Eq.(2.1.6)). However, this does not compare well with experiment at all. For example, the ionization potential of Helium is ~ 23.4 eV, which means that it takes a photon with an energy of at least 23.4 eV to ionize a Helium atom :

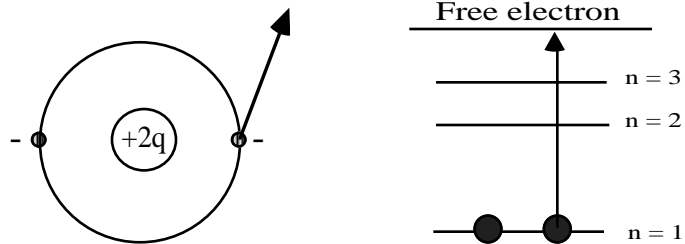


This suggests that the 1s level of a Helium atom has an energy of - 23.4 eV and not - 54.4 eV as the simple argument would suggest. How could we be off by over 30 eV ? It is because we did not account for the other electron in Helium. If we were to measure the energy that it takes to remove the second electron from He^+



the result (known as the second ionization potential) is indeed close to 54.4 eV. But the (first) ionization potential is about 30 eV less indicating that it takes 30eV less energy to pull an electron out of a neutral Helium atom than it takes to pull an electron out of a Helium ion He^+ that has already lost one electron. The reason is that an electron in a Helium atom feels a repulsive force from the other electron, which effectively raises its energy by 30 eV and makes it easier for it to escape.

Fig.3.1.1. Ionization of a neutral Helium atom takes approximately 23.4 eV of energy suggesting that the $n=1$ level has an energy of - 23.4 eV.



In general, the ionization levels for multielectron atoms can be calculated approximately from the Schrodinger equation by adding to the nuclear potential $U_{\text{nuc}}(\vec{r})$, a "self-consistent" field $U_{\text{scf}}(\vec{r})$ due to the other electrons (Fig.3.1.2):

$$U(\vec{r}) = U_{\text{nuc}}(\vec{r}) + U_{\text{scf}}(\vec{r}) \quad (3.1.2)$$

For Helium, the nuclear potential arises from the nuclear charge of '+Zq' located at the origin and is given by $U_{\text{nuc}}(\vec{r}) = -Zq^2 / 4\pi\epsilon_0 r$. The self-consistent field arises from the other ($Z-1$) electrons, since an electron does not feel any potential due to itself. In order to calculate the potential $U_{\text{scf}}(r)$ we need the electronic charge which depends on the wavefunctions of the electron which in turn has to be calculated from the

Schrodinger equation containing $U_{\text{scf}}(\mathbf{r})$. This means that the calculation has to be done self-consistently.

- Step 1 :** Guess electronic potential $U_{\text{scf}}(\vec{r})$
- Step 2 :** Find eigenfunctions and eigenvalues from Schrodinger equation.
- Step 3 :** Calculate the electron density, $n(\vec{r})$
- Step 4 :** Calculate the electronic potential $U_{\text{scf}}(\vec{r})$.
- Step 5 :** If the new $U_{\text{scf}}(\vec{r})$ is significantly different from last guess, update $U_{\text{scf}}(\vec{r})$ and go back to Step 2. If the new $U_{\text{scf}}(\vec{r})$ is within say 10 meV of the last guess, the result has converged and the calculation is complete.

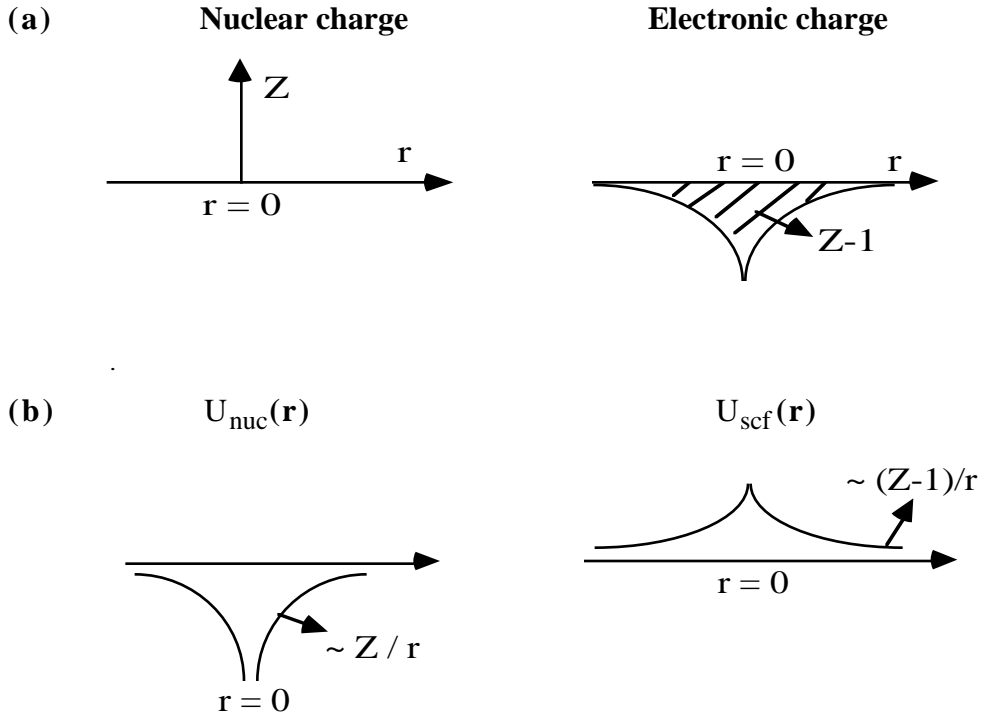


Fig.3.1.2. Sketch of the (a) nuclear charge density and the electronic charge density, (b) potential energy felt by an additional electron due to the nucleus, $U_{\text{nuc}}(\mathbf{r})$, and the other electrons, $U_{\text{scf}}(\mathbf{r})$. The latter has to be calculated self-consistently.

For **Step 2** we can use essentially the same method as we used for the hydrogen atom, although an analytical solution is usually not possible. The potential $U_{\text{scf}}(\vec{r})$ is in general not isotropic (which means independent of θ, ϕ) but for atoms it can be assumed to be isotropic without incurring any significant error. However, the dependence on 'r' is quite complicated so that no analytical solution is possible. Numerically, however, it is just as easy to solve the Schrodinger equation with any $U(r)$ as it is to solve the hydrogen atom problem with $U(r) \sim 1/r$.

For **Step 3** we have to sum up the probability distributions for all the occupied eigenstates :

$$n(\vec{r}) = \sum_{\text{occ } \alpha} |\Phi_{\alpha}(\vec{r})|^2 = \sum_{\text{occ } n,l,m} \left| \frac{f_n(r)}{r} \right|^2 |Y_{lm}(\theta, \phi)|^2 \quad (3.1.3)$$

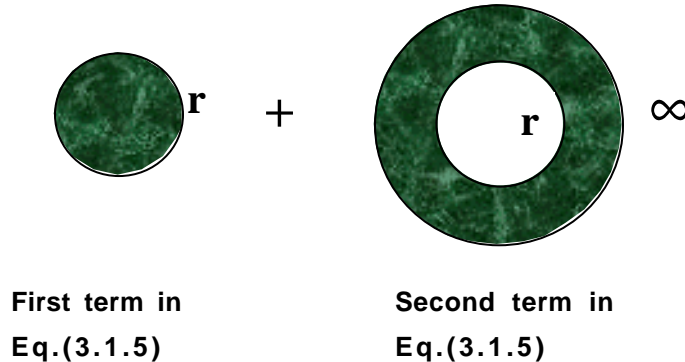
If we assume the charge distribution to be isotropic (independent of θ, ϕ), we can write

$$\sigma(r) \equiv \int r^2 \sin \theta d\theta d\phi n(\vec{r}) = \sum_{\text{occ } n,l,m} |f_n(r)|^2 \quad (3.1.4)$$

For **Step 4** we can use straightforward electrostatics to show that

$$U_{\text{scf}}(r) = \frac{Z-1}{Z} \left[\frac{q^2}{4\pi\epsilon_0 r} \int_0^r dr' \sigma(r') + \frac{q^2}{4\pi\epsilon_0} \int_r^{\infty} dr' \frac{\sigma(r')}{r'} \right] \quad (3.1.5)$$

The two terms in Eq.(3.1.5) arise from the contributions due to the charge within a sphere of radius 'r' and that due to the charge outside of this sphere as shown below.



The first term is the potential at 'r' outside a sphere of charge which can be shown to be the same as if the entire charge were concentrated at the center of the sphere:

$$\frac{q^2}{4\pi\epsilon_0 r} \int_0^r dr' \sigma(r')$$

The second term is the potential at 'r' inside a sphere of charge and can be shown to be the same as the potential at the center of the sphere (the potential is the same at all points inside the sphere since the electric field is zero)

$$\frac{q^2}{4\pi\epsilon_0} \int_r^\infty dr' \frac{\sigma(r')}{r'}$$

Adding the two components we obtain the total potential.

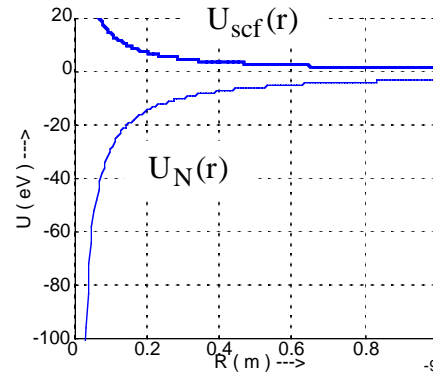
To understand the reason for the factor $(Z-1)/Z$ in Eq.(3.1.4), we note that the appropriate charge density for each eigenstate should exclude the eigenstate under consideration, since no electron feels any repulsion due to itself. For example, Silicon has 14 electrons $1s^2 2s^2 2p^6 3s^2 3p^2$ and the self-consistent field includes all but one of these electrons - for the 3p level we exclude the 3p electron, for the 3s level we exclude the 3s electron etc. However, it is more convenient to simply take the total charge density and scale it by the factor $(Z-1)/Z$. This preserves the spherical symmetry of the charge distribution and the difference is usually not significant. Note that the total electronic charge is equal to Z :

$$\int_0^\infty dr \sigma(r) = \sum_{\text{occ. } n,l,m} 1 = Z \quad (3.1.6)$$

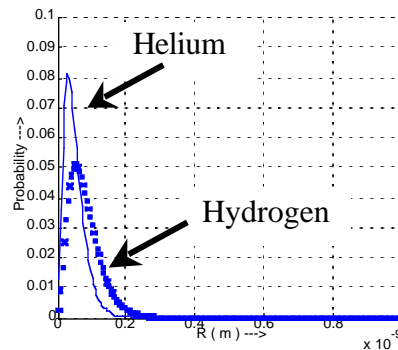
since the radial eigenfunctions are normalized : $\int_0^\infty dr |f_n(r)|^2 = 1$.

Helium atom: Fig.3.1.3 shows the potential profile and the probability distribution for the 1s state of Helium obtained using the self-consistent field method we have just described. Also shown for comparison is the 1s level of the Hydrogen atom, discussed in the last chapter.

Fig.3.1.3. Self-consistent field method applied to the Helium atom. (a) Nuclear potential, $U_N(r)$ and the self-consistent electronic potential $U_{scf}(r)$.

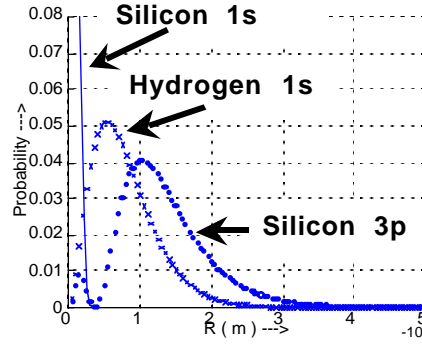


(b) Radial probability distribution for the 1s state in Helium and Hydrogen.



Silicon atom: Fig.3.1.4 shows the probability distribution for the 1s and 3p states of Silicon obtained using the self-consistent field method. Also shown for comparison is the 1s level of the Hydrogen atom. Note that the Silicon 1s state is very tightly confined relative to the 3p state or the Hydrogen 1s state. This is typical of core states and explains why such states remain well-localized in solids, while the outer electrons (like 3p) get delocalized.

Fig.3.1.4. Self-consistent field method applied to the Silicon atom. Radial probability distribution for Hydrogen 1s level, Silicon 1s level and 3p level.



3.2. Relation to the multielectron picture

Multielectron Schrodinger equation: It is important to recognize that the self-consistent field method is really an approximation that is widely used only because the correct method is virtually impossible to implement. For example, if we wish to calculate the eigenstates of a Helium atom with two electrons we need to solve a two-electron Schrodinger Equation of the form

$$E \Psi(\vec{r}_1, \vec{r}_2) = \left(-\frac{\hbar^2}{2m} \nabla^2 + U(\vec{r}_1) + U(\vec{r}_2) + U_{ee}(\vec{r}_1, \vec{r}_2) \right) \Psi(\vec{r}_1, \vec{r}_2) \quad (3.2.1)$$

where \vec{r}_1 and \vec{r}_2 are the coordinates of the two electrons and U_{ee} is the potential energy due to their mutual repulsion : $U_{ee}(\vec{r}_1, \vec{r}_2) = e^2 / 4\pi\epsilon_0 |\vec{r}_1 - \vec{r}_2|$. This is more difficult than it is to solve the "one-electron" Schrodinger equation that we have been talking about, but it is not impossible. However, this approach quickly gets out of hand as we go bigger atoms with many electrons and so is seldom implemented directly. But suppose we could actually calculate the energy levels of multielectron atoms. How would we use our results (in principle, if not in practice) to construct a **one-electron energy level diagram** like the ones we have been drawing? The answer depends on what we want our one-electron energy levels to tell us.

Ionization levels and affinity levels: Our interest is primarily in describing the flow of current, which involves inserting an electron and then taking it out or vice versa, as we discussed in our introductory Chapter. So we would want the one-electron energy levels to represent either the energies needed to take an electron out of the atom (ionization levels) or the energies involved in inserting an electron into the atom (affinity levels).

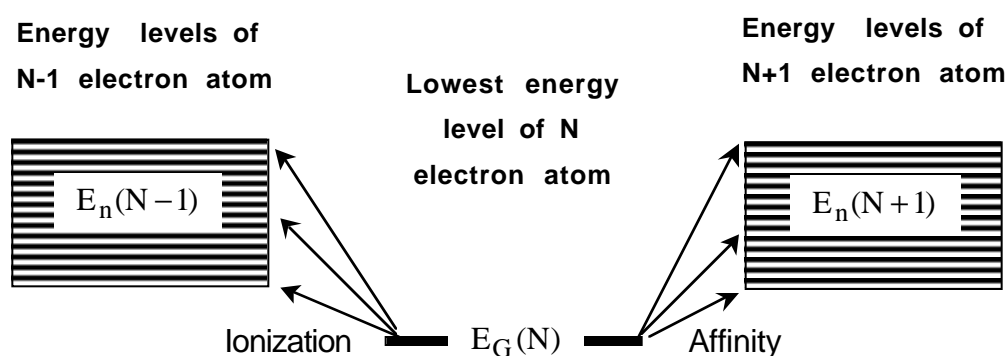


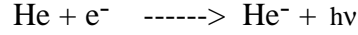
Fig.1.3.1. One-electron energy levels represent energy differences between the energy levels of the N-electron atom and the (N-1) or the (N+1) electron atom. The former, called the ionization levels, are the filled states from which an electron can be removed, while the latter, called the affinity levels, are the empty states to which an electron can be added.

For the ionization levels, the one electron energies ϵ_n represent the difference between the ground state energy $E_G(N)$ of the neutral N-electron atom and the nth energy level, $E_n(N-1)$ positively ionized (N-1)-electron atom:

$$\epsilon_n = E_G(N) - E_n(N-1) \quad (3.2.2a)$$

These ionization energy levels are measured by looking at the photon energy needed to ionize an electron in a particular level. Such photoemission experiments are very useful for probing the occupied energy levels of atoms, molecules and solids. However, they only provide information about the occupied levels, like the 1s level of a Helium atom or the valence band of a semiconductor. To probe the unoccupied levels

like the 2s level of a Helium atom or the conduction band of a semiconductor we need an inverse photoemission experiment like (see Fig.3.2.2)



which measure the affinity of the atom for acquiring additional electrons. To calculate the affinity levels we should look at the difference between the ground state energy $E_G(N)$ and the nth energy level, $E_n(N+1)$ negatively ionized (N+1)-electron atom:

$$\epsilon_n = E_n(N+1) - E_G(N) \quad (3.2.2b)$$

Note that if we want the energy levels to correspond to optical transitions then we should look at the difference between the ground state energy $E_G(N)$ and the nth energy level, $E_n(N)$ of the N-electron atom, since visible light does not change the total number of electrons in the atom, just excites them to a higher energy.

$$\epsilon_n = E_n(N) - E_G(N)$$

There is no a priori reason why the energy gap obtained from this calculation should correspond to the energy gap obtained from either the ionization or the affinity levels. In large solids (without significant excitonic effects) we are accustomed to assuming that the optical gap is equal to the gap between the valence and conduction bands, but this need not be true for small nanostructures.

Single-electron charging energy: As we have explained above, the straightforward approach for calculating the energy levels would be to calculate the energies $E_G(N)$ and $E_n(N \pm 1)$ from an N-electron and an (N±1) electron Schrodinger equation (cf. Eq.(3.2.1) which is a two-electron Schrodinger equation) respectively. This, however, is usually impossible and the only practical approach for large atoms, molecules or solids is to include an effective potential $U_{\text{scf}}(\vec{r})$ in the Schrodinger Equation as we have been discussing.

How do we choose this effective potential? If we use $U_{ee}(N)$ to denote the total electron-electron interaction energy of an N-electron system then the appropriate U_{scf} for the ionization levels is equal to the change in the interaction energy as we go from an N-electron to an (N-1)-electron atom:

$$[U_{\text{scf}}]_{\text{ionization}} = U_{\text{ee}}(N) - U_{\text{ee}}(N-1) \quad (3.2.3a)$$

Similarly the appropriate U_{scf} for the affinity levels is equal to the change in the interaction energy between an N-electron and an (N+1)-electron atom:

$$[U_{\text{scf}}]_{\text{affinity}} = U_{\text{ee}}(N+1) - U_{\text{ee}}(N) \quad (3.2.3b)$$

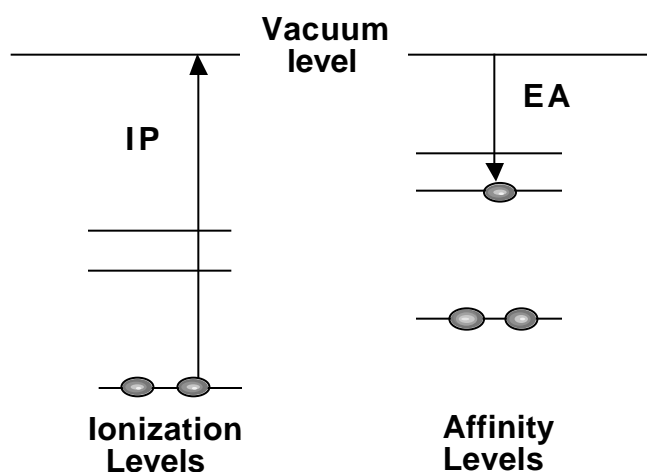
We could write the interaction energy approximately as the electrostatic energy stored in a capacitor $U_{\text{ee}}(N) \rightarrow q^2 N^2 / 2C_E$, corrected to account for the fact that an electron does not interact with itself:

$$U_{\text{ee}}(N) = \frac{q^2}{2C_E} N(N-1) \quad (3.2.4)$$

From Eqs.(3.2.3a,b) and (3.2.4) it is easy to see that

$$[U_{\text{scf}}]_{\text{ionization}} = \frac{q^2}{C_E} (N-1) \quad \text{while} \quad [U_{\text{scf}}]_{\text{affinity}} = \frac{q^2}{C_E} N \quad (3.2.5)$$

Fig.3.2.2. The ionization levels include the repulsive potential from Z-1 electrons while the affinity levels include that of Z electrons, so that the latter is higher in energy by the single-electron charging energy U_0 .

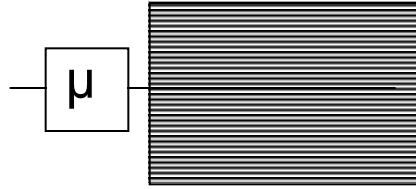


This means that to calculate the ionization levels of a Z -electron atom, we should use the potential due to $(Z-1)$ electrons (one electron for Helium) as we did in the last section. But to calculate the affinity levels we should use the potential due to Z electrons (two electrons for Helium). The energy levels we obtain from the first calculation are lower in energy than those obtained from the second calculation by the single-electron charging energy $U_0 = q^2/C_E$ (see Eq.(3.4.2)) such that

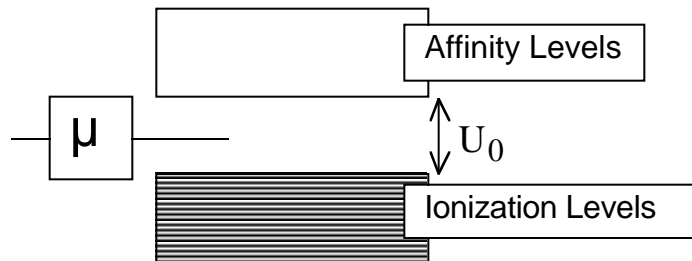
$$\text{Affinity levels} = \text{Ionization Levels} + U_0 \quad (3.2.6)$$

As we discussed in Section I.5, the single-electron charging energy U_0 depends on the degree of localization of the electronic wavefunction and can be several eV in atoms. Even in nanostructures that are say 10 nm or less in dimension, it can be quite significant (that is, comparable to $k_B T$).

One important consequence of this is that even if a structure has energy levels that are very closely spaced compared to $k_B T$,



it may not conduct well, because the one-electron charging effects will create a “Coulomb gap” between the occupied and unoccupied levels:



Of course, this is a significant effect only if the single-electron charging energy U_0 is larger than $k_B T$.

Hartree approximation: In large conductors (large R) U_0 is negligible and the distinction between Z and $(Z-1)$ can be ignored. The self-consistent potential for both ionization and affinity levels is essentially the same and can be written as (cf. Eqs.(3.2.3a) and (3.2.3b)) $U_{\text{scf}} = \partial U_{\text{ee}} / \partial N$ which can be generalized to obtain the standard expression used in density functional theory (DFT):

$$U_{\text{scf}}(\vec{r}) = \frac{\partial U_{\text{ee}}}{\partial [n(\vec{r})]} \quad (3.2.8)$$

which tells us that the self-consistent potential at any point \vec{r} is equal to the change in the electron-electron interaction energy due to an infinitesimal change in the number of electrons at the same point. If we use the standard expression for U_{ee} from classical electrostatics

$$U_{\text{ee}} = \frac{1}{2} \int d\vec{r} \int d\vec{r}' \frac{q^2 n(\vec{r}) n(\vec{r}')}{4\pi\epsilon |\vec{r} - \vec{r}'|} \quad (3.2.9)$$

Eq.(3.2.8) yields the Hartree approximation, $U_{\text{H}}(\vec{r})$ for the self-consistent potential :

$$U_{\text{H}}(\vec{r}) = \int d\vec{r}' \frac{q^2 n(\vec{r}')}{4\pi\epsilon |\vec{r} - \vec{r}'|} \quad (3.2.10)$$

which is a solution of the Poisson equation $-\nabla^2 U_{\text{H}} = q^2 n / \epsilon$ in a homogeneous medium. Device problems often require us to incorporate complicated boundary conditions including different materials with different dielectric constants. It is then more convenient to solve a modified form of the Poisson equation that allows a spatially varying relative permittivity:

$$-\vec{\nabla} \cdot (\epsilon_r \nabla U_{\text{H}}) = q^2 n / \epsilon_0 \quad (3.2.11)$$

But for atoms, there is no complicated inhomogeneity to account for and it is more convenient to work with Eq.(3.2.10).

Correlation energy: The actual interaction energy is less than what Eq.(3.2.9) predicts because electrons can correlate their motion so as to avoid each other - this correlation would be included in a many-electron picture but is missed in the one-particle picture. One way to include it is to write

$$U_{ee} = \frac{1}{2} \int d\vec{r} \int d\vec{r}' \frac{e^2 n(\vec{r})n(\vec{r}') [1 - g(\vec{r}, \vec{r}')] }{4\pi\epsilon |\vec{r} - \vec{r}'|}$$

where g is a correlation function that accounts for the fact that the probability of finding two electrons simultaneously at \vec{r} and \vec{r}' is not just proportional to $n(\vec{r}) n(\vec{r}')$ but is somewhat reduced because electrons try to avoid each other (actually this correlation factor is spin-dependent, but we are ignoring such details). The corresponding self-consistent potential is also reduced (cf.Eq.(3.2.10)):

$$U_{scf} = \int d\vec{r}' \frac{e^2 n(\vec{r}') [1 - g(\vec{r}, \vec{r}')] }{4\pi\epsilon |\vec{r} - \vec{r}'|} \quad (3.2.12)$$

A lot of research has gone into estimating the function $g(\vec{r}, \vec{r}')$ (generally referred to as the exchange-correlation "hole").

The basic effect of the correlation energy is to add a **negative** term $U_{xc}(\vec{r})$ to the Hartree term $U_H(\vec{r})$ discussed above (cf. Eq.(3.2.10)) :

$$U_{scf}(\vec{r}) = U_H(\vec{r}) + U_{xc}(\vec{r}) \quad (3.2.13)$$

One simple approximation, called the local density approximation (LDA) expresses U_{xc} at a point in terms of the electron density at that point:

$$U_{xc}(\vec{r}) = -\frac{q^2}{4\pi\epsilon_0} C [n(\vec{r})]^{1/3} \quad (3.2.14)$$

Here, C is a constant of order 1. The physical basis for this approximation is that an individual electron introduced into a medium with a background electron density $n(r)$ will push other electrons in its neighborhood creating a positive correlation "hole" around it. If we model this hole as a positive sphere of radius r_0 then we can estimate

r_0 by requiring that the total charge within the sphere be equal in magnitude to that of an electron:

$$n(r) 4\pi r_0^3 / 3 = 1 \rightarrow r_0 = \frac{1}{C} [n(r)]^{-1/3}$$

C being a constant of order 1. The potential in Eq.(3.2.14) can be viewed as the potential at the center of this positive charge contained in a sphere of radius r_0 :

$$U_{xc}(\vec{r}) = -\frac{q^2}{4\pi\epsilon_0 r_0}$$

Much work has gone into the self-consistent field theory and many sophisticated versions of Eq.(3.2.14) have been developed over the years. But it is really quite surprising that the one-electron picture with a suitable self-consistent field often provides a reasonably accurate description of multielectron systems. The fact that it works so well is not something that can be proved mathematically in any convincing way. Our confidence in the self-consistent field method stems from the excellent agreement that has been obtained with experiment for virtually every atom in the periodic table (see Fig.3.2.3). Almost all the work on the theory of electronic structure of atoms, molecules and solids is based on this method and that is what we will be using.

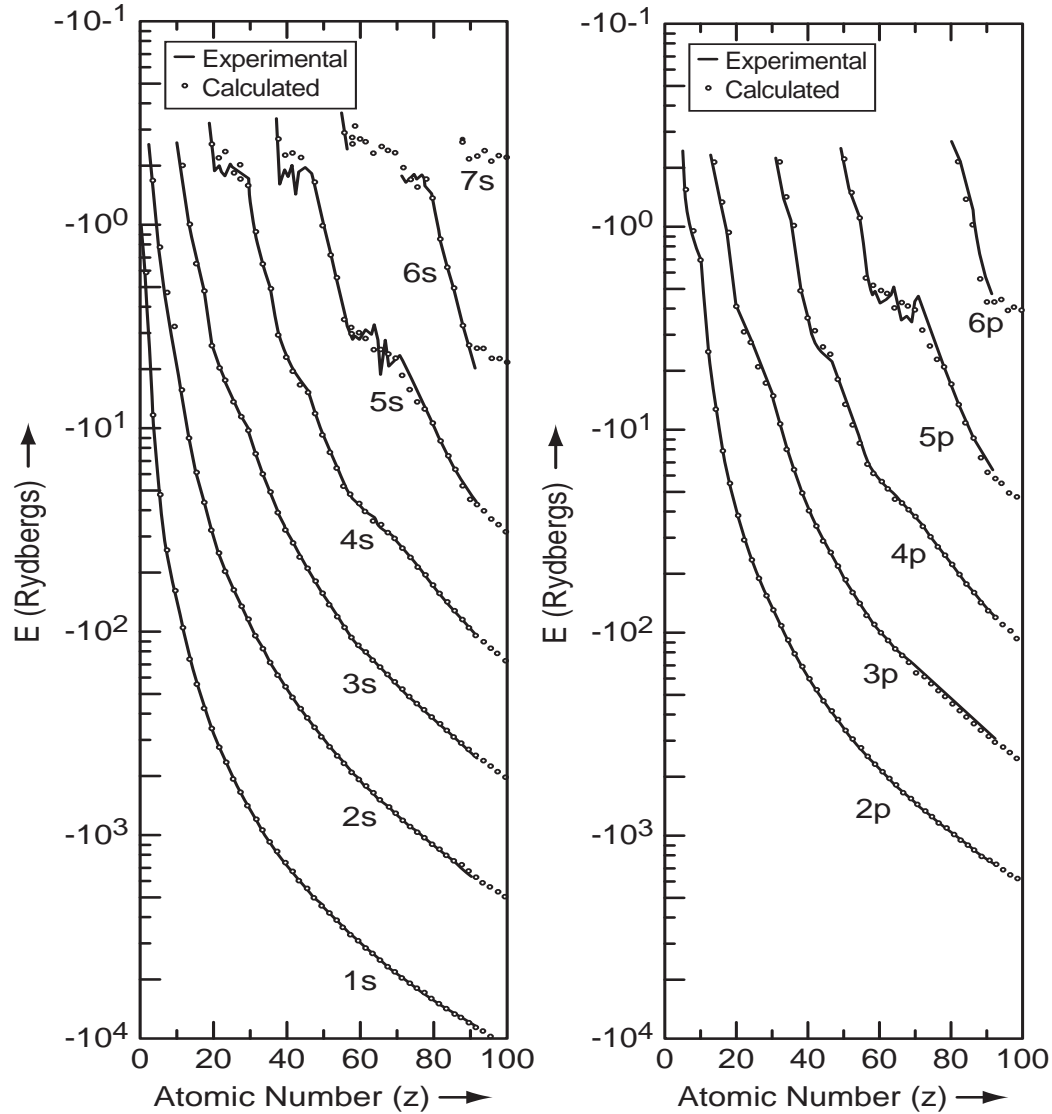


Fig.3.3.3. Energy levels as a function of the atomic number calculated theoretically using a self-consistent field method. The results are in excellent agreement with experiment (adapted from F. Herman and S. Skillman, "Atomic Structure Calculations", p.3-9, Prentice-Hall (1963)). For a hydrogen atom, the 's' and 'p' levels are degenerate (that is, they have the same energy). This is a consequence of the $\sim 1/r$ dependence of the nuclear potential. But this is not true of the self-consistent potential due to the electrons and for multi-electron atoms, the 's' state has a lower energy than the 'p' state.

3.3. Bonding

One of the first successes of quantum theory was to explain the structure of the periodic table of atoms by combining the energy levels obtained from the Schrodinger equation with the Pauli exclusion principle requiring that each level be occupied by no more than one electron. In Section 3.3.1 we will discuss the general trends, especially the periodic character of the energy levels of individual atoms. Based on this understand We will then discuss two mechanisms (ionic and covalent) whereby a pair of atoms, A and B, can lower their overall energy by bonding to form a molecule AB (Sections 3.3.2, 3.3.3): $E(AB) < E(A) + E(B)$.

3.3.1. Valence electrons

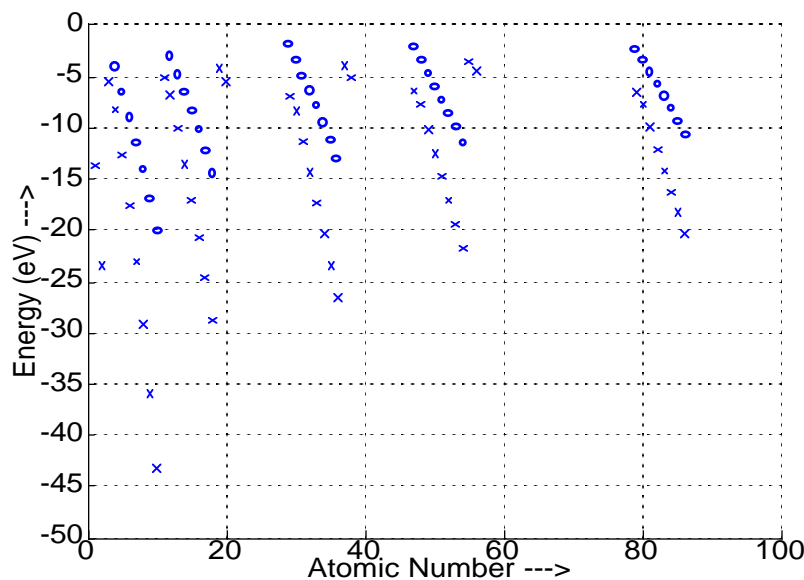


Fig.3.3.1. Energy of the outermost s- (x) and p-levels (o) of the first 86 elements of the periodic table excluding the d- and f-shell transition metals (N = 21-28, 39-46 and 57-78). The numbers are taken from the Solid State Table of the Elements in W.A. Harrison, Electronic Structure and the Properties of Solids, Dover Publications (1989).

It is important to note that only the electrons in the outermost shell, referred to as the valence electrons, participate in the bonding process. The energies of these valence electron exhibit a periodic variation as shown in Fig.3.3.1 for the first eighty-six atoms of the periodic table from Hydrogen (atomic number, N = 1) to Radon

($N=86$), excluding the d- and f-shell transition metals (see Table 2.1). The main point to notice is that the energies tend to go down as we go across a row of the periodic table from Lithium (Li) to Neon (Ne), increases abruptly as we step into the next row with Sodium (Na) and then decreases as we go down the row to Argon (Ar). This trend is shown by both the 's' and 'p' levels and continues onto the higher rows. Indeed this periodic variation in the energy levels is at the heart of the periodic table of the elements.

Table 3.3.1. First eighty-six atoms of the periodic table from Hydrogen (atomic number, $N = 1$) to Radon ($N=86$), excluding the d- and f-shell transition metals ($N = 21-28, 39-46$ and $57-78$).

H										He
(N=1)										(N=2)
Li	Be			B	C	N	O	F	Ne	
(N=3)	(N=4)			(N=5)	(N=6)	(N=7)	(N=8)	(N=9)	(N=10)	
Na	Mg			Al	Si	P	S	Cl	Ar	
(N=11)	(N=12)			(N=13)	(N=14)	(N=15)	(N=16)	(N=17)	(N=18)	
K	Ca	Cu	Zn	Ga	Ge	As	Se	Br	Kr
(N=19)	(N=20)	(N=29)	(N=30)	(N=31)	(N=32)	(N=33)	(N=34)	(N=35)	(N=36)
Rb	Sr	Ag	Zn	In	Sn	Sb	Te	I	Xe
(N=37)	(N=38)	(N=47)	(N=48)	(N=49)	(N=50)	(N=51)	(N=52)	(N=53)	(N=54)
Cs	Ba	Au	Hg	Tl	Pb	B	Po	At	Rn
(N=55)	(N=56)	(N=79)	(N=80)	(N=81)	(N=82)	(N=83)	(N=84)	(N=85)	(N=86)

3.3.2. Ionic bonds

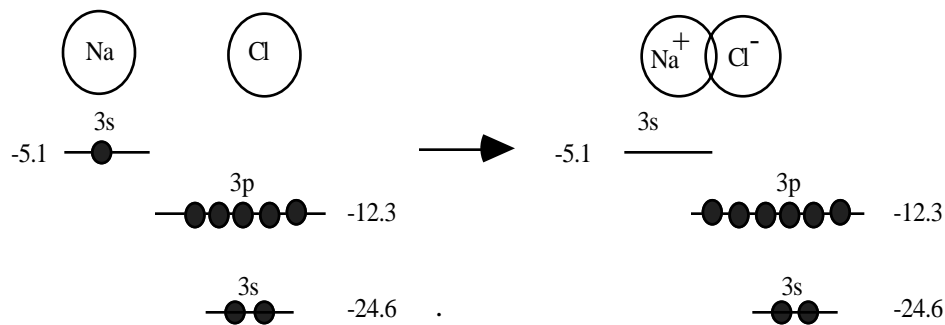


Fig.3.3.2. Formation of Na^+Cl^- from individual Na and Cl atoms with a '3s' electron from Na "spilling over" into the '3p' levels of Cl thereby lowering the overall energy. This is only part of the story, since the overall energetics also includes the electrostatic energy stored in the microscopic capacitor formed by the two ions as explained in the text.

Ionic bonds are typically formed between an atom to the left of the periodic table (like Sodium, Na) and one on the right of the periodic table (like Chlorine, Cl). The energy levels of Na and Cl look roughly as shown in Fig.3.3.2. It seems natural for the '3s' electron from Na to "spill over" into the '3p' levels of Cl thereby lowering the overall energy as shown. Indeed it seems "obvious" that the binding energy, E_{bin} of NaCl would be

$$E_{\text{bin}} = E(\text{Na}) + E(\text{Cl}) - E(\text{Na}^+\text{Cl}^-) = 12.3 - 5.1 = 7.2 \text{ eV}.$$

But this argument is incomplete because we also need to consider the change in the electrostatic energy due to the bonding. The correct binding energy is more like 4 eV,

The point is that the energy levels we have drawn here are all *ionization* levels. The energy needed to create a sodium ion is given by its ionization potential

$$E(\text{Na}^+) - E(\text{Na}) = \text{IP}(\text{Na}) = 5.1 \text{ eV} \quad (3.3.1a)$$

But the energy needed to create a Chlorine ion is given by the *electron affinity* of Cl and this includes an extra charging energy U_0 :

$$E(\text{Cl}) - E(\text{Cl}^-) = \text{EA}(\text{Cl}) = \text{IP}(\text{Cl}) - U_0 = 12.3 \text{ eV} - U_0 \quad (3.3.1b)$$

Combining Eqs.(3.3.1a) and (3.3.1b) we obtain

$$E(\text{Na}) + E(\text{Cl}) - E(\text{Na}^+) - E(\text{Cl}^-) = 7.2 \text{ eV} - U_0 \quad (3.3.2)$$

However, this is not the binding energy of NaCl. It gives us the energy gained in converting neutral Na and neutral Cl into an Na^+ and a Cl^- ion completely separated from each other. If we let an Na^+ and a Cl^- ion that are infinitely far apart come together to form a sodium chloride molecule, Na^+Cl^- , it will gain an energy U_0' in the process.

$$E(\text{Na}^+) + E(\text{Cl}^-) - E(\text{Na}^+\text{Cl}^-) = U_0'$$

so that the binding energy is given by

$$E_{\text{bin}} = E(\text{Na}) + E(\text{Cl}) - E(\text{Na}^+\text{Cl}^-) = 7.2 \text{ eV} - U_0 + U_0' \quad (3.3.3)$$

$U_0 - U_0'$ is approximately 3 eV, giving a binding energy of approximately 4.2 eV. The details of this specific problem are not particularly important – the main point I wish to make is that although the process of bonding by electron transfer may seem like a simple one where one electron “drops” off an atom into another with a lower energy level, the detailed energetics of the process require a more careful discussion. In general, care is needed when using one-electron energy level diagrams to discuss electron transfer on an atomic scale.

3.3.3. Covalent bonds

We have just seen how a lowering of energy comes about when we bring together an atom from the left of the periodic table (like Sodium) and one from the

right (like Chlorine). The atoms on the right of the periodic table have lower electronic energy levels and are said to be more electronegative than those on the left. We would expect electrons to transfer from the higher energy levels in the former to the lower energy levels in the latter to form an ionic bond.

However, this argument does not explain covalent bonds which involve atoms with roughly the same electronegativity. The process is a little more subtle. For example, it is hard to see why two identical 'H' atoms would want to form a H_2 molecule, since no lowering of energy is achieved by transferring an electron from one atom to the other. What happens is that when the two atoms come close together the resulting energy levels split into a bonding level (E_B) and an anti-bonding level (E_A) as shown in Fig.3.3.3. Both electrons occupy the bonding level which has an energy lower than that of an isolated hydrogen atom : $E_B < E_0$

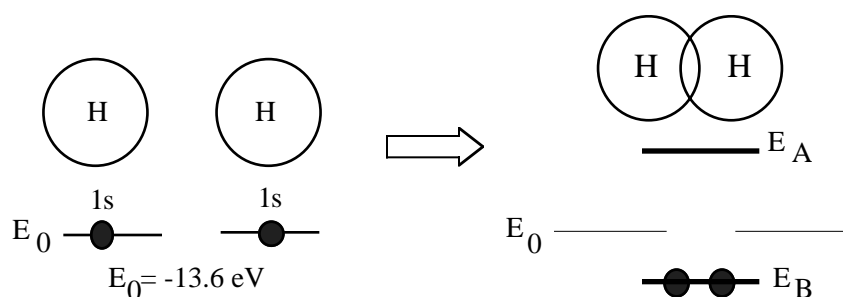


Fig.3.3.3. Formation of H_2 from individual H atoms with a bonding level, E_B and an anti-bonding level, E_A .

How do we calculate E_B ? By solving the Schrodinger equation :

$$E_\alpha \Phi_\alpha(\vec{r}) = \left(-\frac{\hbar^2}{2m} \nabla^2 + U_N(\vec{r}) + U_{N'}(\vec{r}) + U_{scf}(\vec{r}) \right) \Phi_\alpha(\vec{r}) \quad (3.3.4)$$

where $U_N(r)$ and $U_{N'}(r)$ are the potentials due to the left and the right nuclei respectively and $U_{scf}(r)$ is the potential that one electron feels due to the other. To keep things simple let us ignore $U_{scf}(r)$ and calculate the electronic energy levels due to the nuclear potentials alone :

$$E_{\alpha 0} \Phi_{\alpha 0}(\vec{r}) = \left(-\frac{\hbar^2}{2m} \nabla^2 + U_N(\vec{r}) + U_{N'}(\vec{r}) \right) \Phi_{\alpha 0}(\vec{r}) \quad (3.3.5)$$

In Chapter 3 we will show that the lowest energy solution to Eq.(3.3.5) can be written approximately as

$$E_{B0} = E_0 + \frac{a+b}{1+s} \quad (3.3.6)$$

$$\text{where } a = -2E_0 \frac{1 - (1 + \bar{R}) e^{-2\bar{R}}}{\bar{R}}, \quad b = -2E_0 (1 + \bar{R}) e^{-\bar{R}}$$

$$\text{and } s = e^{-\bar{R}} (1 + \bar{R} + (\bar{R}^2/3)), \quad \bar{R} \equiv R/a_0$$

R being the center-to-center distance between the hydrogen atoms

Let us now try to understand the competing forces that lead to covalent bonding. The dashed line in Fig.3.3.4 shows $E_{B0} - E_0$ versus the bond length, R , as given by Eq.(3.3.6). Experimentally, the bond length R for a H_2 molecule is .074 nm, indicating that the overall energy is a minimum for this value of R . Since the energy keeps decreasing as R is decreased, one might wonder why the two hydrogen atoms do not just sit on top of each other ($R = 0$). To answer this question we need to calculate the overall energy which should include the electron-electron repulsion (note that $U_{scf}(r)$ was left out from Eq.(3.3.6)) as well as the nucleus-nucleus repulsion. To understand the overall energetics let us consider the difference in energy between a hydrogen molecule, H_2 and two isolated hydrogen atoms ($2H$).

The energy required to assemble two separate hydrogen atoms from two protons (N, N') and two electrons (e, e') can be written as

$$E(2H) = U_{e,N} + U_{e',N'} = 2 E_0 \quad (3.3.7a)$$

The energy required to assemble an H_2 molecule from two protons (N, N') and two electrons (e, e') can be written as

$$E(H_2) = U_{N,N'} + U_{e,e'} + U_{e,N} + U_{e,N'} + U_{e',N} + U_{e',N'} \quad (3.3.7b)$$

Eq.(3.3.6) gives the quantum mechanical value of $(U_{e,N} + U_{e,N'})$ as well as $(U_{e',N} + U_{e',N'})$ as E_{B0} . Hence

$$E(H_2) = U_{N,N'} + U_{e,e'} + 2 E_{B0} \quad (3.3.7c)$$

The binding energy is the energy it takes to make the hydrogen molecule dissociate into two hydrogen atoms and can be written as

$$E_{\text{bin}} = E(H_2) - E(2H) = 2 (E_{B0} - E_0) + U_{N,N'} + U_{e,e'} \quad (3.3.8)$$

This is the quantity that ought to be a minimum at equilibrium and it consists of three separate terms. Eq.(3.3.6) gives us only the first term. The second term is easily written down since it is the electrostatic energy between the two nuclei which are point charges :

$$U_{N,N'} = q^2 / 4\pi\epsilon_0 R \quad (3.3.9a)$$

The electrostatic interaction between the two electrons should also look like $q^2 / 4\pi\epsilon_0 R$ for large R , but should saturate to $\sim q^2 / 4\pi\epsilon_0 a_0$ at short distances since the electronic charges are diffused over distances $\sim a_0$. Let us approximate it as

$$U_{e,e'} \equiv q^2 / 4\pi\epsilon_0 \sqrt{R^2 + a_0^2} \quad (3.3.9b)$$

noting that this is just an oversimplified approximation to what is in general a very difficult quantum mechanical problem - indeed, electron-electron interactions represent the central outstanding problem in the quantum theory of matter.

The solid line in Fig.3.3.4 shows $U_{N,N'}$ (Eq.(3.3.9a)), while the x's show $U_{e,e'}$ (Eq.(3.3.9b)). The +s shows the total binding energy estimated from Eq.(3.3.8). It has a minimum around 0.1 nm which is not too far from the experimental bond length of 0.074 nm. Also the binding energy at this minimum is ~ 4.5 eV, very close to the actual experimental value. Despite the crudeness of the approximations used, the basic physics of bonding is illustrated fairly well by this example.

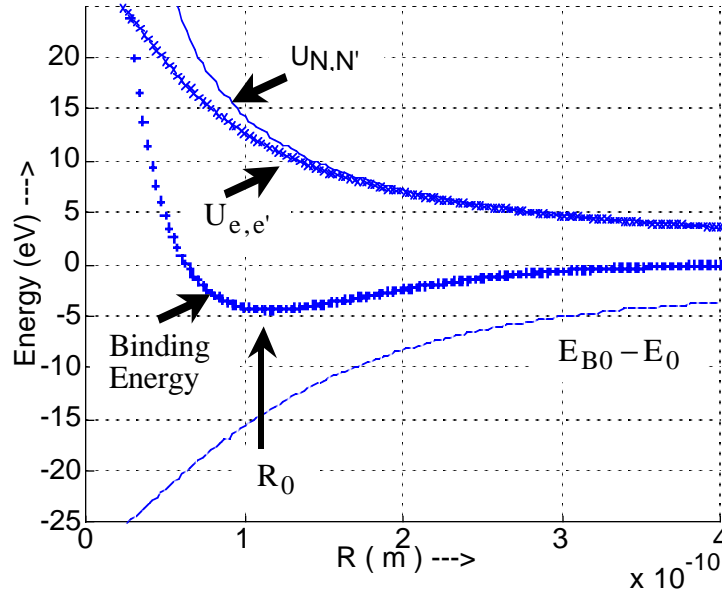


Fig.3.3.4. Various energies as a function of the nuclear distance R

xxxx Approximate electron-electron repulsive energy ($U_{e,e'}$)

Solid line Approximate nucleus-nucleus repulsive energy ($U_{N,N'}$)

Dashed line, ($E_{B0}-E_0$) : Energy of the bonding level in a H_2 molecule relative to the '1s' level in a hydrogen atom calculated approximately from the Schrodinger equation without any self-consistent potential.

++++, Binding energy of a H_2 molecule relative to two hydrogen atoms estimated from $2(E_{B0}-E_0) + U_{N,N'} + U_{e,e'}$.

Vibrational frequency: The shape of the binding energy vs. R curve suggests that we can visualize a hydrogen molecule as two masses connected by a spring.

Fig.3.3.5. A Hydrogen molecule can be viewed as two masses connected by a spring.



An ideal spring with a spring constant K has a potential energy of the form $U(R) = K(R - R_0)^2 / 2$. The binding energy of the hydrogen molecule (see Fig.3.3.4) can be approximated as $U(R) \cong U(R_0) + K(R - R_0)^2 / 2$, where the effective spring constant K is estimated from the curvature $\left[d^2U / dR^2 \right]_{R=R_0}$. Indeed the vibrational frequency $\sqrt{2K/M}$ of the mass and spring system where M is the mass of a hydrogen atom.

Ionization Levels : As we have discussed, the energy levels of a multielectron system usually denote the ionization levels, that is the energy it takes to strip an electron from the system. This means that in the present context the energy level E_B for a hydrogen molecule should represent

$$E_B = E(H_2) - E(H_2^+)$$

Since $E(H_2^+) = U_{N,N'} + U_{e',N} + U_{e',N'}$, we can write using Eq.(3.3.9b),

$$E_B = U_{e,e'} + U_{e,N} + U_{e,N'} = U_{e,e'} + E_{B0} \quad (3.3.10)$$

It is easy to check that for our model calculation (see Fig.3.3.4) E_{B0} is nearly 15 eV below E_0 , but E_B lies only about 4 eV below E_0 . If we were to include a self-consistent field $U_{scf}(r)$ in the Schrodinger equation, we would obtain the energy E_B which would be higher (less negative) than the non-interacting value of E_{B0} by the electron-electron interaction energy $U_{e,e'}$.

Binding energy: It is tempting to think that the binding energy is given by

$$E_{\text{bin}} = 2 (E_{\text{B}} - E_0) + U_{\text{N,N'}}$$

since E_{B} includes the electron-electron interaction energy $U_{\text{e,e'}}$. However, it is easy to see from Eqs.(3.3.8) and (3.3.10) that the correct expression is

$$E_{\text{bin}} = 2 (E_{\text{B}} - E_0) + (U_{\text{N,N'}} - U_{\text{e,e'}})$$

The point I am trying to make is that if we include the electron-electron interaction in our calculation of the energy level E_{B} then the overall energy of two electrons is NOT $2E_{\text{B}}$, for that would double-count the interaction energy between the two electrons. The correct energy is obtained by subtracting off this double-counted part: $2E_{\text{B}} - U_{\text{e,e'}}$.

3.4. Supplementary topic: Multielectron picture

As I mentioned in Section 3.2., the self-consistent field (SCF) method is widely used because the exact method based on a multielectron picture is usually impossible to implement. However, it is possible to solve the multielectron problem exactly if we are dealing with a small channel weakly coupled to its surroundings, like the one-level system discussed in the Prologue (see Section P.4). It is instructive to re-do this one-level problem in the multielectron picture and compare with the results obtained from the SCF method.

One-electron vs. multielectron energy levels: If we have one spin degenerate level with energy ϵ , the one-electron and multielectron energy levels would look as shown in Fig.3.4.1. Since each one-electron energy level can either be empty ('0') or occupied ('1'), multielectron states can be labeled in the form of binary numbers with a number of digits equal to the number of one-particle states. 'N' one-electron states thus give rise to 2^N multielectron states, which quickly diverges as N increases, making a direct treatment impractical. That is why SCF methods are so widely used, even though they are only approximate.

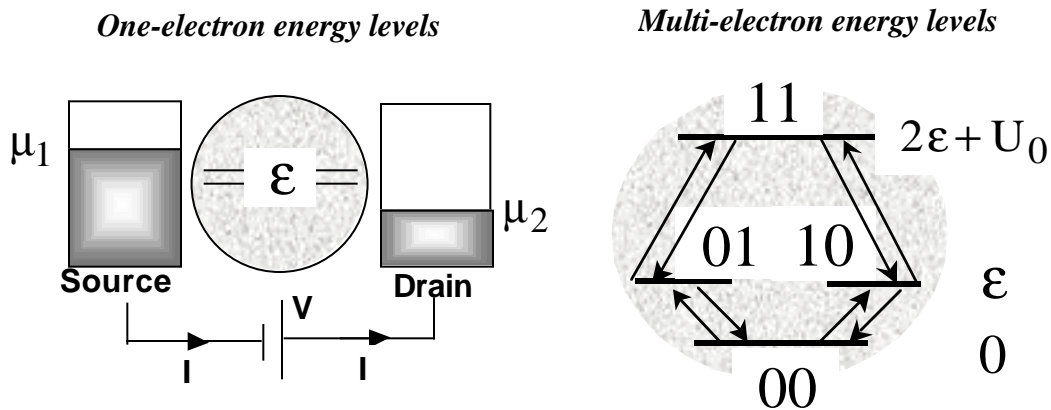


Fig.3.4.1. One-electron vs. multielectron energy levels in a channel with one spin degenerate level having energy ϵ .

For a small system with two one-electron states, there are only four multielectron states: 00, 01, 10 and 11 with energies 0, ϵ , ϵ and $2\epsilon + U_0$ respectively where U_0 is the electron-electron interaction energy associated with the two-electron system. The other states have either zero or one electron and hence do

not involve any interaction energy. In the one-electron picture each state has an average occupation somewhere between 0 and 1.

Master equation: In the multielectron picture, the overall system has different probabilities P_α of being in one of the 2^N possible states α and all the probabilities must add up to one:

$$\sum_{\alpha} P_{\alpha} = 1 \rightarrow P_{00} + P_{01} + P_{10} + P_{11} = 1 \quad (3.4.1)$$

We can calculate the individual probabilities by noting that the system is continually shuffled among these states and under steady state conditions there must be no net flow into or out of any state.

$$\sum_{\beta} R(\alpha \rightarrow \beta) P_{\alpha} = \sum_{\beta} R(\beta \rightarrow \alpha) P_{\beta} \quad (3.4.2)$$

Knowing the rate constants, we can calculate the probabilities by solving Eq.(3.4.2). Equations involving probabilities of different states are called master equations. We could call Eq.(3.4.2) a multielectron master equation.

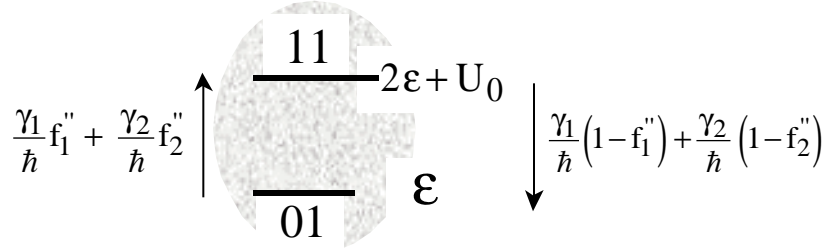
The rate constants $R(\alpha \rightarrow \beta)$ can be written down assuming a specific model for the interaction with the surroundings. For example, if we assume that the interaction only involves the entry and exit of individual electrons from the source and drain contacts then for the '00' and '01' states the rate constants are given by

where $f'_1 \equiv f_0(\epsilon - \mu_1)$ and $f'_2 \equiv f_0(\epsilon - \mu_2)$ (3.4.3a)

tell us the availability of electrons with energy ϵ in the source and drain contacts respectively. The entry rate is proportional to the available electrons, while the exit rate is proportional to the available empty states. The same picture applies to the

flow between the '00' and the '10' states, assuming that up- and down-spin states are described by the same Fermi function in the contacts, as we would expect if each contact is locally in equilibrium.

Similarly we can write the rate constants for the flow between the '01' and the '11' states



$$\text{where } f_1'' \equiv f_0(\epsilon + U_0 - \mu_1) \text{ and } f_2'' \equiv f_0(\epsilon + U_0 - \mu_2) \quad (3.4.3b)$$

tell us the availability of electrons with energy $(\epsilon + U_0)$ corresponding to the energy difference between the 01 and 11 states. This is larger than the energy difference ϵ between the 00 and 01 states because it takes more energy to add an electron when one electron is already present due to the interaction energy $2U_0$.

Using these rate constants it is straightforward to show from Eq.(3.4.2) that

$$\frac{P_{10}}{P_{00}} = \frac{P_{01}}{P_{00}} = \frac{\gamma_1 f_1' + \gamma_2 f_2'}{\gamma_1 (1 - f_1') + \gamma_2 (1 - f_2')} \quad (3.4.4a)$$

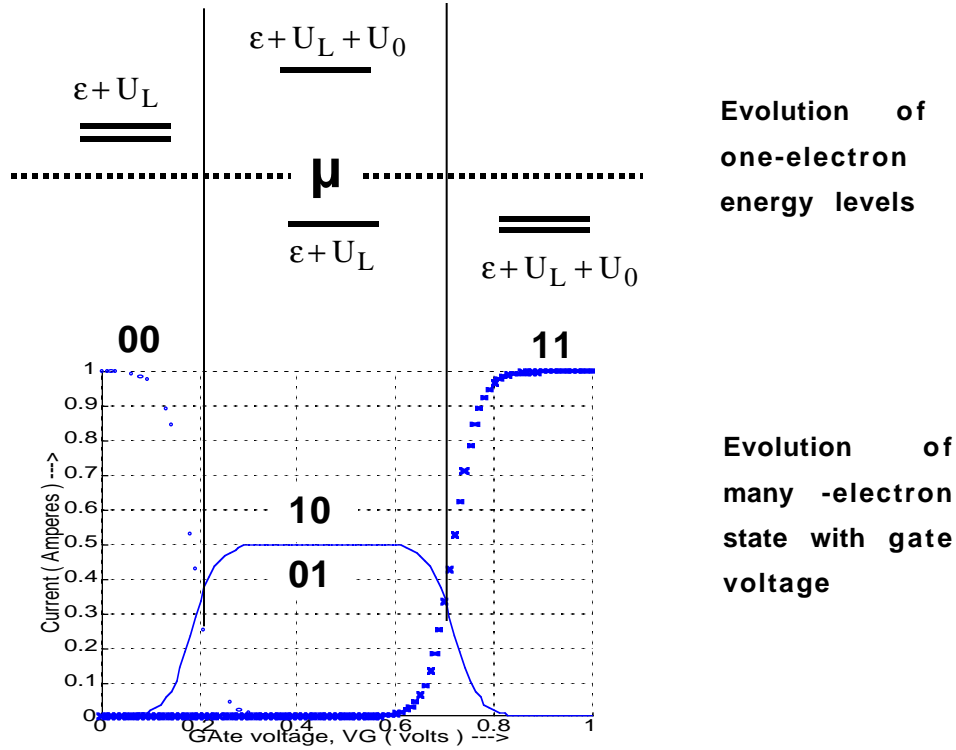
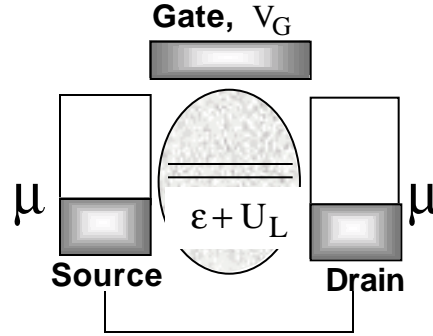
$$\text{and } \frac{P_{11}}{P_{10}} = \frac{P_{11}}{P_{01}} = \frac{\gamma_1 f_1'' + \gamma_2 f_2''}{\gamma_1 (1 - f_1'') + \gamma_2 (1 - f_2'')} \quad (3.4.4b)$$

Together with Eq.(3.4.1), this gives us all the individual probabilities. Fig.3.4.2 shows the evolution of these probabilities as the gate voltage V_G is increased holding the drain voltage V_D equal to zero. The gate voltage shifts the one-electron level $\epsilon \rightarrow \epsilon + U_L$ (we have assumed $U_L = -qV_G$) and the probabilities are calculated from Eqs.(3.4.4) and (3.4.1). The system starts out in the '00' state ($P_{00}=1$), shifts to the '01' and '10' states ($P_{01}=P_{10}=0.5$) once $\epsilon + U_L$ drops below μ , and finally goes into the '11' state ($P_{11}=1$) when $\epsilon + U_L + 2U_0$ drops below μ .

Fig.3.4.2. Evolution of the energy levels of a channel with one spin-degenerate level as the gate voltage V_G is made more positive, holding the drain voltage V_D equal to zero.

$$\mu = 0, \epsilon = 0.2 \text{ eV}, k_B T = 0.025 \text{ eV}$$

$$U_0 = 0.25 \text{ eV}, U_L = -q V_G$$



Relation between the multielectron picture and the one-electron levels: As I have emphasized in Section 2.2, one-electron energy levels represent *differences* between energy levels in the multielectron picture corresponding to states that differ by *one electron*. Transitions involving the addition of one electron are called *affinity* levels while those corresponding to the removal of one electron are called *ionization*

levels. For example (see Fig.3.4.2), if the system is in the '00' state then there are two degenerate one-electron levels $\varepsilon + U_L$ representing

$$\varepsilon + U_L = E(10) - E(00) = E(01) - E(00) \quad \text{Affinity levels}$$

Once it is in the '10' state there are two one-electron levels

$$\varepsilon + U_L = E(10) - E(00) \quad \text{Ionization level}$$

$$\text{and} \quad \varepsilon + U_L + U_0 = E(11) - E(10) \quad \text{Affinity level}$$

In the '11' state there are two degenerate one-electron levels

$$\varepsilon + U_L + U_0 = E(11) - E(10) = E(11) - E(01) \quad \text{Ionization levels}$$

Affinity levels lie above μ , while ionization levels lie below μ as shown in Fig.3.4.2. This is a very important general concept regarding the interpretation of the one-electron energy levels when dealing with complicated interacting objects. The occupied (or ionization) levels tell us the energy levels for removing an electron while the unoccupied (or affinity) levels tell us the energy levels for adding an extra electron. Indeed that is exactly how these levels are measured experimentally, the occupied levels by photoemission and the unoccupied levels by inverse photoemission as mentioned in Section 1.1.

Law of equilibrium: Fig.3.4.2 represents an equilibrium calculation with both source and drain contacts having the same Fermi function: $f_1 = f_2$. Equilibrium problems do not really require the use of a master equation like Eq.(3.4.2). We can use the general principle of equilibrium statistical mechanics which states that the probability P_α that the system is in a multielectron state α with energy E_α and N_α electrons is given by

$$P_\alpha = \frac{1}{Z} \exp(-(E_\alpha - \mu N_\alpha)/k_B T) \quad (3.4.5)$$

where the constant Z (called the partition function) is determined so as to ensure that the probabilities of all the states add up to one (Eq.(3.4.5)):

$$Z = \sum_{\alpha} \exp \left(- (E_{\alpha} - \mu N_{\alpha}) / k_B T \right) \quad (3.4.6)$$

This is the central law of equilibrium statistical mechanics that is applicable to any system of particles (electrons, photons, atoms etc), interacting or otherwise [3.4]. The Fermi function is just a special case of this general relation that can be obtained by applying it to a system with just a single one-electron energy level, corresponding to two multielectron states:

α	N_{α}	E_{α}	P_{α}
0	0	0	$1 / Z$
1	1	ϵ	$(1 / Z) \exp [(\mu - \epsilon) / k_B T]$

so that $Z = 1 + \exp [(\mu - \epsilon) / k_B T]$ and it is straightforward to show that the average number of electrons is equal to the Fermi function (Eq.(1.1.1)):

$$N = \sum_{\alpha} N_{\alpha} P_{\alpha} = P_1 = \frac{\exp [(\mu - \epsilon) / k_B T]}{1 + \exp [(\mu - \epsilon) / k_B T]} = f_0 [\epsilon - \mu]$$

For multielectron systems, we can use the Fermi function only if the electrons are not interacting. It is then justifiable to single out one level and treat it independently ignoring the occupation of the other levels. The self-consistent field method uses the Fermi function assuming that the energy of each level depends on the occupation of the other levels. But this is only approximate. The exact method is to abandon the Fermi function altogether and use Eq.(3.4.5) instead to calculate the probabilities of the different multiparticle states.

One well-known example of this is the fact that localized donor or acceptor levels (which have large charging energies U_0) in semiconductors at equilibrium are occupied according to a modified Fermi function (v : level degeneracy)

$$f = \frac{1}{1 + (1/v) \exp((\epsilon - \mu) / k_B T)} \quad (3.4.7)$$

rather than the standard Fermi function (cf. Eq.(P.1.1)). We can easily derive this relation for two spin degenerate levels ($v = 2$) if we assume that the charging energy U_0 is so large that the (11) state has zero probability. We can then write for the remaining states

α	N_α	E_α	P_α
0 0	0	0	1 / Z
0 1	1	ϵ	(1 / Z) $\exp [(\mu - \epsilon)/k_B T]$
1 0	1	ϵ	(1 / Z) $\exp [(\mu - \epsilon)/k_B T]$

so that $Z = 1 + 2 \exp [(\mu - \epsilon)/k_B T]$ and the average number of electrons is given by

$$\begin{aligned}
 N &= \sum_{\alpha} N_{\alpha} P_{\alpha} = P_{01} + P_{10} = \frac{2 \exp [(\mu - \epsilon)/k_B T]}{1 + 2 \exp [(\mu - \epsilon)/k_B T]} \\
 &= \frac{1}{1 + (1/2) \exp [(\epsilon - \mu)/k_B T]}
 \end{aligned}$$

in agreement with Eq.(3.4.7). This result known to every device engineer could thus be viewed as a special case of the general result in Eq.(3.4.5).

Eq.(3.4.5), however, can only be used to treat equilibrium problems. Our primary interest is in calculating the current under non-equilibrium conditions and that is one reason we have emphasized the master equation approach based on Eq.(3.4.2). For equilibrium problems, it gives the same answer. However, it also helps to bring out an important conceptual point. One often hears concerns that the law of equilibrium is a statistical one that can only be applied to large systems. But it is apparent from the master equation approach that the law of equilibrium (Eq.(3.4.5)) is not a property of the system. It is a property of the contacts or the “reservoir”. The only assumptions we have made relate to the energy distribution of the electrons that come in from the contacts. As long as the “reservoirs” are simple, it does not matter how complicated or how small the “system” is.

Current calculation: Getting back to non-equilibrium problems, once we have solved the master equation for the individual probabilities, the source current can be obtained from

$$I_1 = -q \sum_{\beta} (\pm) R_1(\alpha \rightarrow \beta) P_{\alpha} \quad (3.4.8)$$

‘+’ if β has one more electron than α
 ‘-’ if β has one less electron than α

where R_1 represents the part of the total transition rate (R) associated with the source contact. In our present problem this reduces to evaluating the expression

$$\begin{aligned} I_1 = & 2\gamma_1 f_1' P_{00} - \gamma_1 (1 - f_1') (P_{01} + P_{10}) \\ & + 2\gamma_1 f_1'' (P_{01} + P_{10}) - \gamma_1 (1 - f_1'') P_{11} \end{aligned}$$

Fig.3.4.3 shows the current-drain voltage (I - V_D) characteristics calculated assuming that the Laplace potential (Eq.(P.4.1)) is given by $U_L = -q V_D / 2$ with $V_G = 0$. The result is compared with a calculation based on the restricted SCF method described in the last Section. The two approaches agree well for $U_0 = 0.1$ eV, but differ appreciably for $U_0 = 0.25$ eV showing evidence for Coulomb blockade or single-electron charging. An unrestricted SCF method (not shown here) shows better agreement with the exact result, but the degree of agreement depends on the choice of parameters.

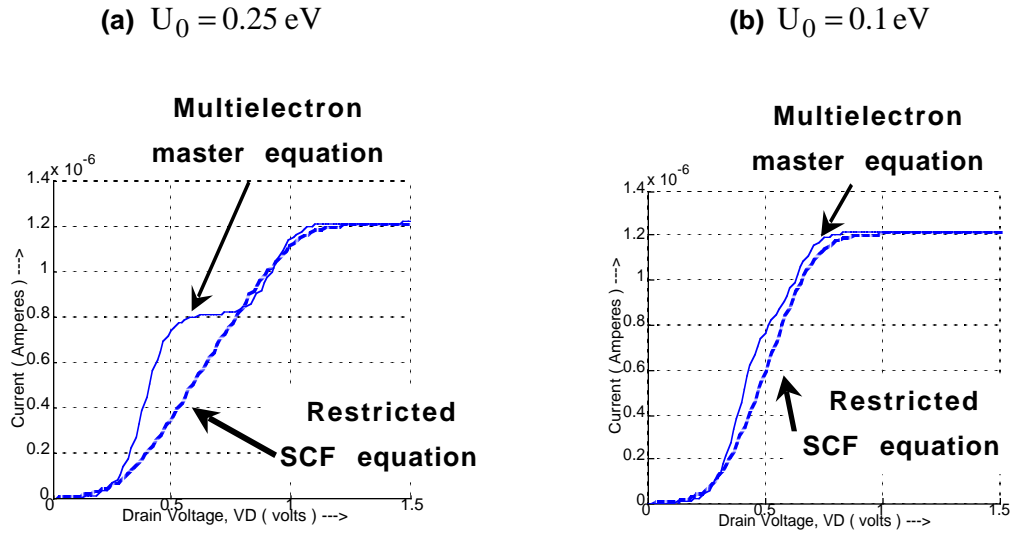


Fig.3.4.3. Current vs, drain voltage V_D calculated assuming $V_G = 0$ with $\mu = 0, \varepsilon = 0.2 \text{ eV}, k_B T = 0.025 \text{ eV}, \gamma_1 = \gamma_2 = 0.005 \text{ eV}, U_L = -qV_D/2$. The two approaches (the self-consistent field and the multielectron master equation) agree well for $U_0 = 0.1 \text{ eV}$, but differ appreciably for $U_0 = 0.25 \text{ eV}$ showing evidence for Coulomb blockade or single-electron charging.

Exercises

E.3.1. Use the self-consistent field method (only the Hartree term) to calculate the energy of the 1s level in a Helium atom. (a) Plot the nuclear potential $U_N(r)$ and the self-consistent electronic potential $U_{scf}(r)$ (cf. **Fig.3.2.1a**). (b) Plot the wavefunction for the 1s level in Helium and compare with that for the 1s level in Hydrogen (cf. **Fig.3.2.1b**).

E.3.2. Use the self-consistent field method (only the Hartree term) to calculate the energies of the 3s and 3p levels in a Silicon atom. (a) Plot the total potential $U(r)=U_{nuc}(r)+U_{scf}(r)$ and compare with that for a Hydrogen atom (cf. **Fig.3.2.2a**). (b) Plot the wavefunction for the 1s and 3p levels in Silicon and compare with that for the 1s level in Hydrogen (cf. **Fig.3.2.2b**).

E.3.3. Plot the approximate binding energy for a Hydrogen molecule as a function of the hydrogen-hydrogen bond length, making use of Eqs.(3.3.6) and (3.3.9) and compare with **Fig.3.3.4**.