Problem 5.7 Suppose you could find a solution $\psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_Z)$ to the Schrödinger (Equation 5.25) for the Hamiltonian in Equation 5.24. Describe how you could construct from it a completely symmetric function and a completely antisymmetric function, which also satisfy the Schrödinger equation, with the same energy.

5.2.1 Helium

After hydrogen, the simplest atom is helium ($Z = 2$). The Hamiltonian,

$$ H = \left\{ -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{1}{4\pi\epsilon_0} \frac{2e^2}{r_1} \right\} + \left\{ -\frac{\hbar^2}{2m} \nabla_2^2 - \frac{1}{4\pi\epsilon_0} \frac{2e^2}{r_2} \right\} + \frac{1}{4\pi\epsilon_0} \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}, \quad [5.27] $$

consists of two *hydrogenic* Hamiltonians (with nuclear charge $2e$), one for electron 1 and one for electron 2, together with a final term describing the repulsion of the two electrons. It is this last term that causes all the problems. If we simply *ignore* it, the Schrödinger equation separates, and the solutions can be written as products of *hydrogen* wave functions:

$$ \psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_{nlm}(\mathbf{r}_1)\psi_{n'l'm'}(\mathbf{r}_2), \quad [5.28] $$

only with half the Bohr radius (Equation 4.72), and four times the Bohr energies (Equation 4.70). The total energy would be

$$ E = 4(E_n + E_{n'}), \quad [5.29] $$

where $E_n = -13.6/n^2$ eV. In particular, the ground state would be

$$ \psi_0(\mathbf{r}_1, \mathbf{r}_2) = \psi_{100}(\mathbf{r}_1)\psi_{100}(\mathbf{r}_2) = \frac{8}{\pi a^3} e^{-2(r_1+r_2)/a} \quad [5.30] $$

(see Equation 4.80), and its energy would be

$$ E_0 = 8(-13.6\,\text{eV}) = -109\,\text{eV}. \quad [5.31] $$

Because ψ_0 is a symmetric function, the spin state has to be *antisymmetric*, so the ground state of helium is a *singlet* configuration, with the spins "oppositely aligned". The *actual* ground state of helium is indeed a singlet, but the experimentally determined energy is -78.975 eV, so the agreement is not very good. But this is hardly surprising: We ignored electron repulsion, which is certainly *not* a small contribution. It is clearly *positive* (see Equation 5.27), which is comforting—evidently it brings the total energy up from -109 to -79 eV (see Problem 5.10).

The excited states of helium consist of one electron in the hydrogenic ground state and the other in an excited state:

$$ \psi_{nlm}\psi_{100}. \quad [5.32] $$

[If you try to put *both* electrons in excited states, one immediately drops to the ground state, releasing enough energy to knock the other one into the continuum ($E > 0$), leaving you with a helium *ion* (He^+) and a free electron. This is an interesting system in its own right—see Problem 5.8—but it is not our present concern.] We can construct from this both symmetric and antisymmetric combinations, in the usual way (Equation 5.10); the former go with the *antisymmetric* spin configuration (the singlet), and they are called **parahelium**, while the latter require a *symmetric* spin configuration (the triplet), and they are known as **orthohelium**. The ground state is necessarily parahelium; the excited states come in both forms. Because the symmetric spatial state brings the electrons closer together (as we discovered in Section 5.1.2), we expect a higher interaction energy in parahelium, and indeed it is experimentally confirmed that the parahelium states have somewhat higher energy than their orthohelium counterparts (see Figure 5.2).

Problem 5.8

(a) Suppose you put both electrons in a helium atom into the $n = 2$ state; what would the energy of the emitted electron be?

(b) Describe (quantitatively) the spectrum of the helium ion, He^+.

Problem 5.9 Discuss (qualitatively) the energy level scheme for helium (a) if electrons were identical bosons, and (b) if electrons were distinguishable particles (but still with the same mass and charge). Pretend the electrons still have spin $1/2$.

**Problem 5.10

(a) Calculate $\langle (1/|\mathbf{r}_1 - \mathbf{r}_2|) \rangle$ for the state ψ_0 (Equation 5.30). *Hint*: Do the $d^3\mathbf{r}_2$ integral first, using spherical coordinates and setting the polar axis along $\mathbf{r}_1$, so that

$$|\mathbf{r}_1 - \mathbf{r}_2| = \sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos\theta_2}.$$

The θ_2 integral is easy, but be careful to take the *positive root*. You'll have to break the r_2 integral into two pieces, one ranging from 0 to r_1, the other from r_1 to ∞. *Answer*: $5/4a$.

(b) Use your result in (a) to estimate the electron interaction energy in the ground state of helium. Express your answer in electron volts, and add it to E_0 (Equation 5.31) to get a corrected estimate of the ground-state energy. Compare the experimental value. *Note*: Of course, we're still working with an approximate wave function, so don't expect *perfect* agreement.
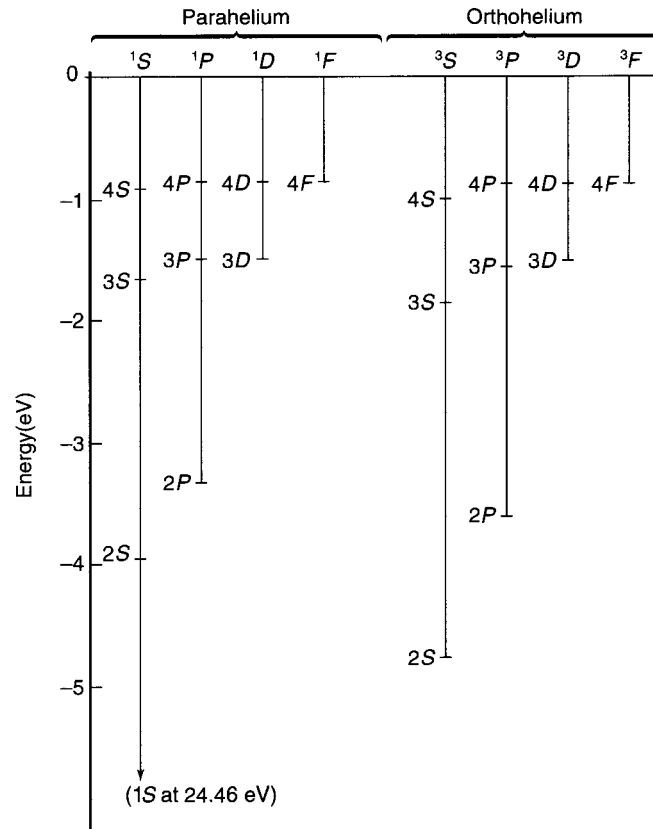
Figure 5.2: Energy level diagram for helium (the notation is explained in Section 5.2.2). Note that parahelium energies are uniformly higher than their orthohelium counterparts. The numerical values on the vertical scale are *relative* to the ground state of ionized helium (He$^+$): $4 \times (-13.6 \text{ eV}) = -54.4$ eV; to get the *total* energy of the state, subtract 54.4 eV.

5.2.2 The Periodic Table

The ground-state electron configurations for heavier atoms can be pieced together in much the same way. To first approximation (ignoring their mutual repulsion altogether), the individual electrons occupy one-particle hydrogenic states (n, l, m), called **orbitals**, in the Coulomb potential of a nucleus with charge Ze. If electrons were bosons (or distinguishable particles), they would all shake down to the ground state $(1,0,0)$, and chemistry would be very dull indeed. But electrons are in fact identical fermions, subject to the Pauli exclusion principle, so only *two* can occupy any given orbital (one with spin up, and one with spin down—or, more precisely, in the

singlet configuration). There are n^2 hydrogenic wave functions (all with the same energy E_n) for a given value of n, so the $n = 1$ **shell** has room for two electrons, the $n = 2$ shell holds eight, $n = 3$ takes 18, and in general the nth shell can accomodate $2n^2$ electrons. Qualitatively, the horizontal rows on the **Periodic Table** correspond to filling out each shell (if this were the whole story, they would have lengths 2, 8, 18, 32, 50, etc., instead of 2, 8, 8, 18, 18, etc.; we'll see in a moment how the electron-electron repulsion throws the counting off).

With helium, the $n = 1$ shell is filled, so the next atom, lithium ($Z = 3$), has to put one electron into the $n = 2$ shell. Now, for $n = 2$ we can have $l = 0$ or $l = 1$; which of these will the third electron choose? In the absence of electron-electron interactions, they both have the same energy (the Bohr energies depend on n, remember, but not on l). But the effect of electron repulsion is to favor the lowest value of l, for the following reason: Angular momentum tends to throw the electron outward (more formally, the expectation value of r increases with increasing l, for a given n), and the farther out an electron gets, the more effectively the inner electrons **screen** the nucleus (roughly speaking, the innermost electron "sees" the full nuclear charge Ze, but the outermost electron sees an effective charge hardly greater than e). Within a given shell, therefore, the state with lowest energy (which is to say, the most tightly bound electron) is $l = 0$, and the energy increases with increasing l. Thus the third electron in lithium occupies the orbital (2,0,0). The next atom (beryllium, with $Z = 4$) also fits into this state (only with "opposite spin"), but boron ($Z = 5$) has to make use of $l = 1$.

Continuing in this way, we reach neon ($Z = 10$), at which point the $n = 2$ shell is filled, and we advance to the next row of the periodic table and begin to populate the $n = 3$ shell. First there are two atoms (sodium and magnesium) with $l = 0$, and then there are six with $l = 1$ (aluminum through argon). Following argon there "should" be 10 atoms with $n = 3$ and $l = 2$; however, by this time the screening effect is so strong that it overlaps the next shell, so potassium ($Z = 19$) and calcium ($Z = 20$) choose $n = 4, l = 0$, in preference to $n = 3, l = 2$. After that we drop back to pick up the $n = 3, l = 2$ stragglers (scandium through zinc), followed by $n = 4, l = 1$ (gallium through krypton), at which point we again make a premature jump to the next row ($n = 5$) and wait until later to slip in the $l = 2$ and $l = 3$ orbitals from the $n = 4$ shell. For details of this intricate counterpoint, refer to any book on atomic physics.[7]

I would be delinquent if I failed to mention the archaic nomenclature for atomic states, because all chemists and most physicists use it (and the people who make up the Graduate Record Exam *love* this kind of thing). For reasons known best to nineteenth-century spectroscopists, $l = 0$ is called s (for "sharp"), $l = 1$ is p (for "principal"), $l = 2$ is d ("diffuse"), and $l = 3$ is f ("fundamental"); after that I guess they ran out of

[7]See, for example, U. Fano and L. Fano, *Basic Physics of Atoms and Molecules* (New York: John Wiley & Sons, 1959), Chapter 18, or the classic by G. Herzberg, *Atomic Spectra and Atomic Structure* (New York: Dover, 1944).

imagination, because the list just continues alphabetically $(g, h, i, \text{etc.})$.[8] The state of a particular electron is represented by the pair nl, with n (the number) giving the shell and l (the letter) specifying the orbital angular momentum; the magnetic quantum number m is not listed, but an exponent is used to indicate the number of electrons that occupy the state in question. Thus the configuration

$$(1s)^2(2s)^2(2p)^2 \qquad [5.33]$$

tells us that there are two electrons in the orbital $(1,0,0)$, two in the orbital $(2,0,0)$, and two in some combination of the orbitals $(2,1,1)$, $(2,1,0)$, and $(2,1,-1)$. This happens to be the ground state of carbon.

In that example there are two electrons with orbital angular momentum quantum number 1, so the total orbital angular momentum quantum number L (capital L, instead of l, to indicate that this pertains to the *total*, not to any one particle) could be 2, 1, or 0. Meanwhile, the two $(1s)$ electrons are locked together in the singlet state, with total spin zero, and so are the two $(2s)$ electrons, but the two $(2p)$ electrons could be in the singlet configuration or the triplet configuration. So the total spin quantum number S (capital, again, because it's the *total*) could be 1 or 0. Evidently the *grand total* (orbital plus spin) J could be 3, 2, 1, or 0. There exist rituals (**Hund's rules**[9]) for figuring out what these totals will be, for a particular atom. The result is recorded as the following hieroglyphic:

$$^{2S+1}L_J \qquad [5.34]$$

(where S and J are the numbers, and L the letter—capitalized, this time, because we're talking about the *totals*). The ground state of carbon happens to be $^3P_0$: The total spin is 1 (hence the 3), the total orbital angular momentum is 1 (hence the P), and the *grand* total angular momentum is zero (hence the 0). In Table 5.1 the individual configurations and the total angular momenta (in the notation of Equation 5.34) are listed, for the first four rows of the Periodic Table.

∗∗∗Problem 5.11

(a) Figure out the electron configurations (in the notation of Equation 5.33) for the first two rows of the Periodic Table (up to neon), and check your results against Table 5.1.

(b) Figure out the corresponding total angular momenta, in the notation of Equation [5.34], for the first four elements. List all the possibilities for boron, carbon, and nitrogen.

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[8]The shells themselves are assigned equally arbitrary nicknames, starting (don't ask me why) with K: the K shell is $n = 1$, the L shell is $n = 2$, M is $n = 3$, and so on (at least they're in alphabetical order).

[9]See, for example, Stephen Gasiorowicz, *Quantum Physics* (New York: John Wiley & Sons, 1974), Chapters 18 and 19.

Table 5.1: Ground-state electron configurations for the first four rows of the Periodic Table.

Z	Element	Configuration	
1	H	$(1s)$	$^2S_{1/2}$
2	He	$(1s)^2$	$^1S_0$
3	Li	(He) $(2s)$	$^2S_{1/2}$
4	Be	(He)$(2s)^2$	$^1S_0$
5	B	(He)$(2s)^2(2p)$	$^2P_{1/2}$
6	C	(He)$(2s)^2(2p)^2$	$^3P_0$
7	N	(He)$(2s)^2(2p)^3$	$^4S_{3/2}$
8	O	(He)$(2s)^2(2p)^4$	$^3P_2$
9	F	(He)$(2s)^2(2p)^5$	$^2P_{3/2}$
10	Ne	(He)$(2s)^2(2p)^6$	$^1S_0$
11	Na	(Ne)$(3s)$	$^2S_{1/2}$
12	Mg	(Ne)$(3s)^2$	$^1S_0$
13	Al	(Ne)$(3s)^2(3p)$	$^2P_{1/2}$
14	Si	(Ne)$(3s)^2(3p)^2$	$^3P_0$
15	P	(Ne)$(3s)^2(3p)^3$	$^4S_{3/2}$
16	S	(Ne)$(3s)^2(3p)^4$	$^3P_2$
17	Cl	(Ne)$(3s)^2(3p)^5$	$^2P_{3/2}$
18	Ar	(Ne)$(3s)^2(3p)^6$	$^1S_0$
19	K	(Ar)$(4s)$	$^2S_{1/2}$
20	Ca	(Ar)$(4s)^2$	$^1S_0$
21	Sc	(Ar)$(4s)^2(3d)$	$^2D_{3/2}$
22	Ti	(Ar)$(4s)^2(3d)^2$	$^3F_2$
23	V	(Ar)$(4s)^2(3d)^3$	$^4F_{3/2}$
24	Cr	(Ar)$(4s)(3d)^5$	$^7S_3$
25	Mn	(Ar)$(4s)^2(3d)^5$	$^6S_{3/2}$
26	Fe	(Ar)$(4s)^2(3d)^6$	$^5D_4$
27	Co	(Ar)$(4s)^2(3d)^7$	$^4F_{9/2}$
28	Ni	(Ar)$(4s)^2(3d)^8$	$^3F_4$
29	Cu	(Ar)$(4s)(3d)^{10}$	$^2S_{1/2}$
30	Zn	(Ar)$(4s)^2(3d)^{10}$	$^1S_0$
31	Ga	(Ar)$(4s)^2(3d)^{10}(4p)$	$^2P_{1/2}$
32	Ge	(Ar)$(4s)^2(3d)^{10}(4p)^2$	$^3P_0$
33	As	(Ar)$(4s)^2(3d)^{10}(4p)^3$	$^4S_{3/2}$
34	Se	(Ar)$(4s)^2(3d)^{10}(4p)^4$	$^3P_2$
35	Br	(Ar)$(4s)^2(3d)^{10}(4p)^5$	$^2P_{3/2}$
36	Kr	(Ar)$(4s)^2(3d)^{10}(4p)^6$	$^1S_0$

(c) **Hund's first rule** says that, all other things being equal, the state with the highest total spin will have the lowest energy. What would this predict in the case of the excited states of helium?

(d) Hund's second rule says that if a subshell (n, l) is no more than half filled, then the lowest energy level has $J = |L - S|$; if it is more than half filled, then $J = L + S$ has the lowest energy. Use this to resolve the boron ambiguity in (b).

(e) Use Hund's rules and the fact that a symmetric spin state must go with an antisymmetric position state (and vice versa) to resolve the carbon ambiguity in (b). What can you say about nitrogen?

Problem 5.12 The ground state of dysprosium (element 66, in the sixth row of the Periodic Table) is listed as $^5I_8$. What are the total spin, total orbital, and grand total angular momentum quantum numbers? Suggest a likely electron configuration for dysprosium.

5.3 SOLIDS

In the solid state, a few of the loosely bound outermost **valence** electrons in each atom become detached and roam around throughout the material, no longer subject only to the Coulomb field of a specific "parent" nucleus, but rather to the combined potential of the entire crystal lattice. In this section we will examine two extremely primitive models: first, the electron gas theory of Sommerfeld, which ignores *all* forces (except the confining boundaries), treating the wandering electrons as free particles in a box (the three-dimensional analog to an infinite square well); and second, Bloch's theory, which introduces a periodic potential representing the electrical attraction of the regularly spaced, positively charged, nuclei (but still ignores electron-electron repulsion). These models are no more than the first halting steps toward a quantum theory of solids, but already they reveal the critical role of the Pauli exclusion principle in accounting for the "solidity" of solids, and provide illuminating insight into the remarkable electrical properties of conductors, semiconductors, and insulators.

5.3.1 The Free Electron Gas

Suppose the object in question is a rectangular solid, with dimensions l_x, l_y, l_z, and imagine that an electron inside experiences no forces at all, except at the impenetrable walls:

$$V(x, y, z) = \begin{cases} 0, & \text{if } (0 < x < l_x, 0 < y < l_y, 0 < z < l_z); \\ \infty, & \text{otherwise.} \end{cases} \qquad [5.35]$$

The Schrödinger equation,

$$-\frac{\hbar^2}{2m}\nabla^2\psi = E\psi,$$