16 Atoms and Molecules

This chapter begins by showing how QM explains the structure and basic properties of multielectron atoms and their position in the periodic table of elements. It then looks at the different types of forces that bind atoms together to form molecules, and at the long-range intermolecular forces that are responsible for many of the chemical properties of matter, and more generally play a crucial role in physics, chemistry and biology. In the final section, the properties of atomic nuclei are shown to reveal an internal structure with periodicities reminiscent of those of atoms.

When we turn our attention to the structure of the atom, we encounter a complex mathematical problem (all too familiar from classical physics), namely the many-body problem. Dealing with molecules, which are usually made up of many atoms, introduces further complications. But little by little, and year by year, our ability to deal with such problems has improved thanks to the development of various specially designed approximation methods, the most important of which are discussed in this chapter, with a focus on the simplest, diatomic molecules. Of course, things have changed radically with the advent of the computer; relatively simple systems, such as atoms with not too many electrons, can now be studied with precision. In quantum chemistry, however, in particular when dealing with systems of larger size, computational approaches face significant challenges due to the complexity arising from the exponential growth of the system's wave function with each added particle. More modern computational techniques using efficient quantum algorithms are expected to have runtimes and resource requirements that scale polynomially with system size and desired accuracy, making it possible to carry out complex calculations involving large molecules.

16.1 Multielectron Atoms. The Hartree–Fock Method

Solving the problem of a system of many electrons in the presence of nuclei is central to much of physics and chemistry. Since the many-body problem does not in general admit of an exact solution, approximate methods must be used to study such systems. The most important such method for solving the Schrödinger equation for systems with more than one electron, and in general for complicated atomic, molecular, and nuclear problems, is the self-consistent field method, which was proposed in its intuitive form by Hartree[1] in 1928 and further developed by Fock in 1930 taking into account the antisymmetry of the electron wave functions.

[1] Douglas Rayner Hartree (1897–1958) was an English mathematician and physicist, best known for developing numerical analysis and its application to atomic structure calculations.

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Taking the atomic case as an example, the basic idea of the Hartree–Fock method is that it considers that each electron moves in a mean field produced by the other electrons and the nucleus and, in turn, contributes to the effective field felt by the other electrons. As they are simpler (though less accurate), we will first derive Hartree's atomic equations and then correct them.

Consider an atom with N electrons. The Hamiltonian of the kth electron coupled to the nucleus is $\widehat{H}_0(\mathbf{r}_k)$, but the Coulomb repulsion couples it to the rest of the electrons, and so the total Hamiltonian of the atom (neglecting spin–orbit coupling) becomes

$$H = \sum_k \widehat{H}_0(\mathbf{r}_k) + \sum_{k<l} V(\mathbf{r}_k, \mathbf{r}_l) = \sum_k \widehat{H}_0(\mathbf{r}_k) + \tfrac{1}{2} \sum_{l \neq k} V(\mathbf{r}_k, \mathbf{r}_l). \tag{16.1}$$

To apply the variational method (see Section 13.8), we propose as the initial test function the product of N independent-particle wave functions,

$$\psi(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \varphi_1(\mathbf{r}_1)\varphi_2(\mathbf{r}_2) \ldots \varphi_N(\mathbf{r}_N). \tag{16.2}$$

The expectation value of the Hamiltonian calculated with this wave function is

$$\langle \widehat{H} \rangle = \sum_k \int \varphi_k^* \widehat{H}_0 \varphi_k \, d^3 r_k + \tfrac{1}{2} \sum_{l \neq k} \int \varphi_k^* \varphi_l^* V(\mathbf{r}_k, \mathbf{r}_l) \varphi_k \varphi_l \, d^3 r_k \, d^3 r_l. \tag{16.3}$$

We want this quantity to be stationary (in fact, to be a minimum) against arbitrary small changes of the test function. If the φ_k^* are varied, leaving the φ_k fixed, this implies

$$\delta \langle \widehat{H} \rangle = \sum_k \int \delta \varphi_k^* \left[\widehat{H}_0 + \sum_{l \neq k} \langle l | V(k,l) | l \rangle \right] \varphi_k \, d^3 r_k = 0. \tag{16.4}$$

However, the $\delta \varphi_k^*$ are not independent, since from the condition that the norm of each wave function does not change it follows that

$$\int \delta \varphi_k^* \varphi_k d^3 r_k = 0. \tag{16.5}$$

To take these restrictions into account when calculating $\delta \langle \widehat{H} \rangle$ we apply the method of indeterminate Lagrange multipliers by multiplying (16.5) by the undetermined constant E_k and subtracting the sum of all these expressions from Eq. (16.4). This gives

$$\sum_k \int \delta \varphi_k^* \left[\widehat{H}_0 + V_k - E_k \right] \varphi_k \, d^3 r_k = 0, \tag{16.6}$$

with

$$V_k = \sum_{l \neq k} \langle l | V(k,l) | l \rangle = \sum_{l \neq k} \int \varphi_l^* V(\mathbf{r}_k, \mathbf{r}_l) \varphi_l \, d^3 r_l. \tag{16.7}$$

$V_k(\mathbf{r}_k)$ represents the average potential at the position of electron k, produced by the other electrons. Since in (16.6) the arbitrary variations $\delta \varphi_k^*$ can already be considered independent, the following system of Hartree equations must be satisfied

$$(\widehat{H}_0 + V_k)\varphi_k = E_k \varphi_k. \tag{16.8}$$

Each Hartree equation is the Schrödinger equation for an atomic electron moving in the field produced by the nucleus (interaction contained in $\widehat{H}_0$) and the mean-field

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potential V_k produced by the other electrons. We see that the procedure has allowed us to formally transform the problem of N coupled particles into N one-particle problems.

The main drawback of this method is that the exclusion principle has not been taken into account. This was corrected by Fock[2], replacing the test function (16.2) by the corresponding fully antisymmetrized function, including the spinor dependence. In the notation used in Chapter 15,

$$\Psi(\xi_1, \ldots, \xi_N) = \sum_{P_k} \widehat{P}_k a_{P_k} \varphi_1(\xi_1)\varphi_2(\xi_2) \ldots \varphi_N(\xi_N). \tag{16.9}$$

The calculation is complicated, but it can be done explicitly. In the absence of spin–orbit coupling, one obtains a system of orbital equations analogous to the previous one, the so-called Fock–Dirac equations or Hartree–Fock equations,

$$(\widehat{H}_0 + V_k)\varphi_k - \sum_{l \neq k} V_{kl}\varphi_l = E_k \varphi_k, \tag{16.10}$$

where

$$V_{kl} = \int \varphi_k^* V(k,l)\varphi_l \, d^3 r_l = \langle k | V(k,l) | l \rangle \tag{16.11}$$

is the exchange potential, the meaning of which was discussed in Section 15.3. A comparison with the Hartree equations shows that the latter are obtained from the Fock–Dirac equations by neglecting the exchange effects.

Both the Hartree and the Fock–Dirac equations are integrodifferential, since the effective potentials are only known once the solutions are known. The numerical procedure proposed by Hartree to solve them consists of finding a self-consistent solution by iteration, as follows. An initial selection of test functions $\varphi_k^{(0)}$ is used for a first approximate calculation of the potentials V_k and V_{kl}. These are introduced into the system of equations, which is solved to obtain a new approximation to the wave functions, $\varphi_k^{(1)}$. With these new values, the effective potentials are recalculated and the process is repeated, to obtain $\varphi_k^{(2)}$. The procedure is continued until the resulting wave functions match (within acceptable errors) those entered in the previous step. Once these solutions are determined, the energy is calculated using the formula

$$E = \sum_k E_k - \tfrac{1}{2} \sum_k \sum_{l \neq k} \left[\langle kl | \widehat{V}(k,l) | kl \rangle - \langle kl | \widehat{V}(k,l) | lk \rangle \right], \tag{16.12}$$

which is obtained by taking the dot product of Eq. (16.10) with φ_k and summing over k. The E_k represent an approximation to the ionization energy associated with each electron.

This method was successfully applied by Fock as early as 1934 to the Li and Na atoms, and is widely used today to solve problems of atomic structure. Assuming that each electron moves in the mean central field produced by the nucleus and the other orbiting electrons, the electronic states can be described with the quantum numbers n, l, m and s_3 used for the hydrogen-like states. This means that the atom is considered to have a well-defined total angular momentum and, in the approximation in which spin–orbit coupling can be neglected, both the orbital and the spinorial atomic

[2] Vladimir Alexandrovich Fock (or Fok) (1898–1974) was an outstanding Russian-Soviet theoretical physicist and mathematician; about a dozen subjects are named in his honor.

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momentum are well defined (this is particularly the case for light atoms). However, the fact that the effective potential differs significantly from a simple Coulomb potential implies that the energy of the electron depends both on the principal quantum number n (defined as $l + 1+$ number of nodes of the radial function) and on the orbital momentum l. Thus, the energy of the atom depends in a rather complicated way on the electronic quantum numbers.

On the other hand, the requirement that the atom must not contain two electrons in the same state (n, l, m, s_3), according to the exclusion principle, implies that as we add electrons to successively build the different atoms, we must increase the value of n from the lowest possible value $n = 1$ to a maximum that depends on the total number of electrons to be accommodated. From experience with hydrogen-like wave functions, we know that the energy of the electron increases as n increases. This fact, which is universal (for fixed l), leads to the observation that the physical and chemical properties of atoms do not change continuously as the atomic number Z (the number of protons in the nucleus) increases. When the addition of a new electron makes it necessary to assign a higher value to n, an obvious discontinuity appears. This observation is verified in practice and forms the basis of the periodic table of the elements proposed by Mendeleev[3] in 1869, as we shall see in the next section. With the advent of QM the periodic table took on the value of a structural arrangement.

The conclusion is that the classification of atomic electrons according to the value of the principal quantum number n is fundamental and expresses in synthetic terms a set of atomic properties.

16.1.1 Atomic shell structure

The preceding discussion suggests the introduction of the concept of (atomic) shells, a notion proposed by Bohr: all the electrons with the same n are found in the same shell. A shell is full (or closed) if it contains as many electrons as the exclusion principle allows. The shells are denoted by the corresponding value of n, or alternatively by the notation introduced by X-ray spectroscopy, namely,

n	1	2	3	4	5	6	7
Shell	K	L	M	N	O	P	Q

Within each shell, electrons can have integer values of l ranging from 0 to $n-1$, forming the subshells s, p, d, f, with $l = 0, 1, 2, 3$, respectively. To determine the number of electrons that fit in a subshell, we note that in each state with fixed n, l, m there can be two electrons, associated with the two possible values of s_3. Therefore, the total number of electrons in the subshells s, p, d, f, is 2, 6, 10, 14, respectively. If all atomic wave functions were hydrogen-like, this would give $2n^2$ electrons per shell. However, this is not the case in real atoms, where only the subshells s, p, d, and f exist, so a shell never contains more than 32 (2+6+10+14) electrons when it is full, as shown in Table 16.1.

[3] Dmitri Ivanovich Mendeleyev (better known as Dmitri Mendeleev) (1834–1907) was a Russian chemist, best known for his observation and development of the periodic classification of the (chemical) elements. He knew and classified about 70 elements and predicted the existence of another 10.

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Table 16.1 Electronic configuration and spectroscopic notation of the atomic elements. Transition metal groups: (1) Fe group, (2) Pd group, (3) lanthanoid or rare earth group, (4) Pt group, (5) actinoid group.

Z	Element	Configuration	SN $n=1$	$l=s$	2 $s\ p$	3 $s\ p\ d$	4 $s\ p\ d\ f$	5 $s\ p\ d\ f$	6 $s\ p\ d\ f$	7 $s\ p$	Shell
1	H	$1s$	$^2S_{1/2}$	1							K
2	He	$1s^2$	$^1S_0$	2							
3	Li	He$2s$	$^2S_{1/2}$	2	1						
4	Be	He$2s^2$	$^1S_0$	2	2						
5	B	He$2s^2 2p$	$^2P_{1/2}$	2	2 1						
⋮											
10	Ne	He$2s^2 2p^6$	$^1S_0$	2	2 6						
11	Na	Ne$3s$	$^2S_{1/2}$	2	2 6	1					M
12	Mg	Ne$3s^2$	$^1S_0$	2	2 6	2					
13	Al	Ne$3s^2 3p$	$^2P_{1/2}$	2	2 6	2 1					
⋮											
18	Ar	Ne$3s^2 3p^6$	$^1S_0$	2	2 6	2 6					
19	K	Ar$4s$	$^2S_{1/2}$	2	2 6	2 6	1				N
20	Ca	Ar$4s^2$	$^2S_0$	2	2 6	2 6	2				
21	Sc	Ar$fs^2 3d$	$^2D_{3/2}$	2	2 6	2 6 1	2	} 1)			
⋮											
30	Zn	Ar$4s^2 3d^{10}$	$^1S_0$	2	2 6	2 6 10	2				
31	Ga	Ar$4s^2 3d^{10} 4p$		2	2 6	2 6 10	2 1				
⋮											
36	Kr	Ar$4s^2 3d^{10} 4p^6$	$^1S_0$	2	2 6	2 6 10	2 6				
37	Ru	Kr$5s$		$^2S_{1/2}$	2	2 6	2 6 10	2 6	1		O
38	Sr	Kr$5s^2$	$^1S_0$	2	2 6	2 6 10	2 6	2			
39	Y	Kr$5s^2 4d$	$^2D_{3/2}$	2	2 6	2 6 10	2 6 1	2	} 2)		
⋮											
48	Cd	Kr$5s^2 4d^{10}$	$^1S_0$	2	2 6	2 6 10	2 6 10	2			
49	In	Kr$5s^2 4d^{10} 5p$	$^2P_{1/2}$	2	2 6	2 6 10	2 6 10	2 1			
⋮											
54	Xe	Kr$5s^2 4d^{10} 5p^6$	$^1S_0$	2	2	2 6 10		2 6 10	2 6		
55	Cs	Xe$6s$	$^2S_{1/2}$	2	2 6	2 6 10	2 6 10	2 6	1		P
56	Ba	X$36s^2$	$^1S_0$	2	2 6	2 6 10	2 6 10	2 6	2		
57	La	Xe$6s^2 5d$	$^2D_{3/2}$	2	2 6	2 6 10	2 6 10	2 6	2		
58	Ce	Xe$6s^2 4f 5d$	$^3H_5$	2	2 6	2 6 10	2 6 10 1	2 6	2	} 3)	
⋮											
71	Lu	Xe$6s^2 4f^{14} 5d$	$^2D_{3/2}$	2	2 6	2 6 10	2 6 10 14	2 6 1	2		
72	Hf	Xe$6s^2 4f^{14} 5d^2$	$^3F_2$	2	2 6	2 6 10	2 6 10 14	2 6 2	2	} 4)	
⋮											
80	Hg	Xe$6s^2 4f^{14} 5d^{10}$	$^1S_0$	2	2 6	2 6 10	2 6 10 14	2 6 10	2		
81	Tl	Xe$6s^2 4f^{14} 5d^{10} 6p$	$^2P_{1/2}$	2	2 6	2 6 10	2 6 10	14	2 6 10	2 1	
⋮											
86	Rn	Xe$6s^2 4f^{14} 5d^{10} 6p^6$	$^1S_0$	2	2 6	2 6 10	2 6 10 14	2 6 10	2 6		
87	Fr	Rn$7s$	$^2S_{1/2}$	2	2 6	2 6 10	2 6 10 14	2 6 10	2 6	1	Q
88	Ra	Rn$7s^2$	$^1S_0$	2	2 6	2 6 10	2 6 10 14	2 6 10	2 6	2	
89	Ac	Rn$7s^2 6d$	$^2D_{3/2}$	2	2 6	2 6 10	2 6 10 14	2 6 10	2 6 1	2	
90	Th	Rn$7s^2 6d^2$	$^3F_2$	2	2 6	2 6 10	2 6 10 14	2 6 10	2 6 2	2	
91	Pa	Rn$7s^2 5f 26d$	$^4K_{11/2}$	2	2 6	2 6 10	2 6 10 14	2 6 10	2 6 2	2	} 5)
⋮											
103	Lw	Rn$7s^2 5f^{14} 6d$		2	2 6	2 6 10	2 6 10 14	2 6 10 14	2 6 1	2	

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The order in which the layers and subshells are filled as Z increases depends on the interactions between the electrons, with the tendency to fill the lower energy levels first. Thus, the first shells to be filled are $n = 1, 2, 3, \ldots$, but as n increases, additional values of l appear and since the energy of the electrons depends on both n and l, there are states that appear in the reverse order to that expected, as shown in Table 16.1. These inversions are important, as we will see later, because filling the $3d, 4d, 5d$ subshells produces the transition metals (38 in total), while the filling of the $4f, 5f$ subshells (which opens space for 14 elements each) produces the lanthanides and actinides, respectively. The inversions are due to the fact that the outer shell of an atom in its ground state can only contain s and p electrons, so the d and f subshells are filled as inner subshells, increasing their energy.

The notation used in Table 16.1 to specify the electronic configuration of the orbitals is $(nl)^k$ or simply nl^k to refer to k equivalent electrons in the nl state. In the spectroscopic notation a so-called term $^{2S+1}L_j$ is introduced, which specifies the quantum numbers of the angular state of the atom. For example, the ground state of H is $^2\mathrm{S}_{1/2}$, while that of He is $^1\mathrm{S}_0$. The correspondence between the electronic configuration and the spectroscopic name (the term) is not straightforward and is determined by means of Hund's empirical rules proposed by Friedrich Hund (1896–1997) during 1925, according to which the state with the largest s and the largest L (for this s) has the lowest energy.

16.2 The Periodic Table of the Elements

Table 16.2 contains all the presently known chemical elements up to number 118,[4] the heaviest element. The table shows how the electronic subshells fill up as the atomic number increases, forming the nine traditional groups (the columns of the table, numbered from 0 to VIII; the present-day, upgraded table contains 18 groups), and seven periods (the rows of the table, numbered from 1 to 7, corresponding to the shells K, L,... Q). The elements are arranged in the order of increasing atomic number Z, and each group contains chemically similar elements.

As we move from left to right in the table, that is, as the layers are filled, there is a gradual evolution of the chemical and physical properties of the elements, showing the periodicities discovered by Mendeleev. We will briefly discuss these properties in what follows and refer the interested reader to specialized texts for more detailed description.

Most of the elements in the table (about 80%) are metals; another seven are considered metalloids (or semi-metals, such as Si, Ge, etc., which have properties between metals and nonmetals); the rest are nonmetals. Metals are good conductors of heat and electricity (have high conductivity), while nonmetals are insulators (poor conductors of heat and electricity). A semiconductor is a material with a conductivity between conductors and insulators, as discussed in Section 6.3. In chemistry a metal is defined

[4] For decades, the table contained the "natural" elements, the last one being ^{92}U (uranium); now the table contains several additional elements up to (currently) ^{118}Og (oganesson), an extremely short-lived noble gas produced at the Joint Institute for Nuclear Research (JINR) in Dubna, Russia. In fact, all the "new" elements are produced in large accelerators.

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Table 16.2 Periodic table of the elements. For each shell, the orbitals beyond the inert gas shell, that is, beyond the upper closed shell, are given. For example, the electronic configuration of $_{11}$Na is (Ne)(3s)=$(1s)^2(2s)^2(2p)^6(3s)$.

Periodic Table of Elements

atomic number
Symbol
atomic standard weight

1 H 1.0080																	2 He 4.0026
3 Li 6.94	4 Be 9.0122											5 B 10.81	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.180
11 Na 22.990	12 Mg 24.305											13 Al 26.982	14 Si 28.085	15 P 30.974	16 S 32.06	17 Cl 35.45	18 Ar 39.95
19 K 39.098	20 Ca 40.078	21 Sc 44.956	22 Ti 47.867	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.845	27 Co 58.933	28 Ni 58.693	29 Cu 63.546	30 Zn 65.38	31 Ga 69.723	32 Ge 72.63	33 As 74.922	34 Se 78.971	35 Br 79.904	36 Kr 83.798
37 Rb 85.468	38 Sr 87.62	39 Y 88.906	40 Zr 91.224	41 Nb 92.906	42 Mo 95.95	43 Tc [98]	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29
55 Cs 132.91	56 Ba 137.33	57-71	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po [209]	85 At [210]	86 Rn [222]
87 Fr [223]	88 Ra [226]	89-103	104 Rf [267]	105 Db [268]	106 Sg [269]	107 Bh [270]	108 Hs [269]	109 Mt [277]	110 Ds [281]	111 Rg [282]	112 Cn [285]	113 Nh [286]	114 Fl [290]	115 Mc [290]	116 Lv [293]	117 Ts [294]	118 Og [294]

57 La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm [145]	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.05	71 Lu 174.97	lanthanoids
89 Ac [227]	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np [237]	94 Pu [244]	95 Am [243]	96 Cm [247]	97 Bk [247]	98 Cf [251]	99 Es [252]	100 Fm [257]	101 Md [258]	102 No [259]	103 Lr [262]	actinoids

as an element that can easily form positive ions by losing electrons (cations) and tends to form metallic bonds. A metallic bond is formed by the valence electrons moving freely through the metal lattice. The valence electrons are those in the outermost shell of an atom, so they can be transferred to or shared with another atom to form bonds. Chemically, metals react with oxygen to form a metal oxide; a metal oxide reacts with water to form a base.

To the left of the table, essentially in the columns Ia–IIIa, are the most electropositive metals, containing one to three electrons in their outer layer, which they can easily transfer in an electrovalent bond, thus becoming ions (cations) with a noble-gas configuration. Those in column Ia are the so-called alkali metals (Li, Na, K, …, used in the Stern–Gerlach experiments precisely because they have only one outer electron and a ground state $^2S_{1/2}$). The alkaline earth metals, contained in group IIa, are all divalent. At the other end of the table, especially at the top, are the nonmetals (acid-forming elements); they need one or more electrons to close their outer shell, so they participate with negative ionic valence. These properties are even more pronounced in the halogens (F, Cl, Br, I, At), contained in column VIIb, which, lacking a single electron to complete their outer shell, easily form ionic compounds with alkali metals, known as salts (LiF, NaCl, KCl, etc.). Among the halogens, F is the most electronegative element (the concept of electronegativity, introduced by Pauling,[5] refers to the ability of an atom in a molecule to attract electrons). The complete transfer of valence electrons between atoms gives rise to ionic bonding between two oppositely charged ions. For example, in NaCl, the Na loses its single outer electron (becoming Na^+), which is captured by the Cl to complete its outer shell (becoming Cl^-).

From columns Ia to VIIb of the table there is a gradual transition from the more metallic to the less metallic elements. The elements in the middle region of the table have intermediate properties. In particular, in the first two periods, C and Si (which belong to group IVb) have four electrons in their outer shell (valence 4) and do not donate or accept electrons, they share pairs of electrons, forming covalent rather than ionic compounds (see Section 16.4).

The number of electrons an atom gives up or gains (number of valence bonds) to achieve a stable molecular configuration is called valence. Covalency is the maximum number of covalent bonds an atom can form within a molecule using its empty orbitals; for example, the covalency of carbon is 4.

The longer periods (4, 5, 6) in the intermediate region contain the transition metals, which include the series of Fe (from Sc to Zn), Pd (from Y to Cd), and Pt (from Hf to Tl) (the classification varies somewhat from author to author). The transition metals differ from the electropositive metals in several properties, such as the multiplicity of valences, the formation of covalent bonds, and so on. The metals of groups Ib–IIIb have one to three electrons more than a pseudo-rare gas (i.e., a configuration corresponding to a rare gas plus a complete d-subshell). However, the metals of group Ib (Cu, Ag, and Au, which belong to the so-called noble metals) can use electrons from the d-subshell to form compounds, making them di- and trivalent, as well as

[5] Linus Pauling (1901–1994) was a prominent US-born chemical engineer, chemist, biochemist and notorious peace activist for nuclear disarmament; he was awarded the Nobel Prize for Chemistry in 1954 and the Nobel Peace Prize in 1962.

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monovalent. Group IVb and Vb elements include semimetals (or semiconductors), which have transitional properties between one class and another.

The rare gases, members of group 0, form a separate class. These elements, also known as noble gases, are chemically inert because all their layers are closed. Finally, we have the internal transition metals, the lanthanides and actinides, which are chemically equivalent to La and Ac, respectively, because they are formed by filling an inner layer close to the nucleus, while the outer layer (also incomplete) remains essentially the same. The 14 lanthanides extend from lanthanum (Z=57) to lutetium (Z=71); the 14 actinides start with actinium (Z=89) and end with lawrencium (Z=103).

There are alternative forms of the periodic table. Among the best known is the grouping based on electronic structure proposed by Thomsen (1895) and Bohr (1922); it is a geometric rearrangement of Table 16.2, relatively easy to understand from the point of view of the previous discussion.

16.3 The Helium Atom

The theoretical study of the He atom – the simplest element after H – is of great importance, since it represents a crucial test for Schrödinger's theory, as Bohr's theory could not deal with it. The He atom has been studied extensively and, although it can only be solved by approximate methods, highly accurate solutions are now available. The remarkable agreement between the theoretical and experimental results confirms beyond doubt the validity of the theoretical description. More specifically, it confirms that the electromagnetic interaction is the only one that plays a relevant role in atomic structure.

To solve the general n-electron problem, one proceeds as follows. The motion of the center of mass (CM) is irrelevant to the analysis, so it can be omitted from the description. If $\mathbf{r}_{ei}$ is the position of electron i (i=1, 2,…, n) with mass m_e, and $\boldsymbol{r}_0$ is the position of the nucleus with mass M, then the coordinate of the center of mass is given by

$$\boldsymbol{R} = \frac{M\boldsymbol{r}_0 + m_e \sum_i^n \boldsymbol{r}_{ei}}{M + nm_e}. \tag{16.13}$$

The Schrödinger equation for the system of $n+1$ particles is rewritten in terms of the relative coordinates $\boldsymbol{r}_i = \boldsymbol{r}_{ei} - \boldsymbol{r}_0$, under the hypothesis that the potential depends only on the latter. The resulting equation contains the CM motion in separable form and can be eliminated as was done, for example, in Section 12.1 in connection with the H problem. The result is a Schrödinger equation for the relative motion of n bodies of reduced mass $m = \left(M^{-1} + \sum m_i^{-1}\right)^{-1}$,

$$-\frac{\hbar^2}{2m}\sum_{i=1}^{n}\nabla_i^2\psi - \frac{\hbar^2}{M}\sum_{i>j}^{n}\left(\frac{\partial^2}{\partial x_i \partial x_j} + \frac{\partial^2}{\partial y_i \partial y_j} + \frac{\partial^2}{\partial z_i \partial z_j}\right)\psi + V\psi = E\psi. \tag{16.14}$$

This equation shows that the movement of the nucleus produces two different effects. The first consists in replacing the mass of the electron by its reduced mass and, although

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it depends on the isotope, it is the same for all energy levels. The second effect exists only if $n > 1$ (so it occurs in He, but not in H) and generates a correction to the energy that is given to first order in perturbation theory by (see Eq. (13.18))

$$\delta E = \frac{1}{M} \sum_{i>j} \langle p_{x_i} p_{x_j} + p_{y_i} p_{y_j} + p_{z_i} p_{z_j} \rangle, \tag{16.15}$$

and therefore depends on the state under consideration. In the case of the He atom, for example, this correction essentially only affects the p-states and also depends on the symmetry of the orbital wave function, that is on the total spin. In other words, it is a small additional correction due to the interaction between the electrons, which is essentially an exchange effect. However, since it is a small disturbance (of the order of m/M), we will disregard it from now on and consider only the mass correction.

In the approximation just discussed, the Hamiltonian of the helium-like atom with two electrons and arbitrary Z (neglecting relativistic, spin-orbit, and other small corrections) is

$$\widehat{H} = \frac{\hat{p}_1^2}{2m} + \frac{\hat{p}_2^2}{2m} - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|}. \tag{16.16}$$

The eigenvalues and eigenfunctions of this Hamiltonian are determined by approximation methods. The most accurate results are obtained using the variational method but, as we will see later, even a crude perturbative approximation gives acceptable results. Before carrying out detailed calculations, however, we will determine the qualitative structure of the He spectrum. To do this, we neglect in Eq. (16.16) the repulsive interaction potential between the two electrons, thereby transforming the Hamiltonian into the sum of two hydrogen-like Hamiltonians. In this (zero-order) approximation the energy of the system is the sum of the energies of two hydrogen-like electrons, which we will consider in the states (n_1, l_1, m_1) and (n_2, l_2, m_2) (for the moment we ignore the electron spin),

$$E^{(0)} = E_{n1} + E_{n2} = -\tfrac{1}{2}\alpha^2 mc^2 \left(\frac{Z^2}{n_1^2} + \frac{Z^2}{n_2^2} \right) \quad (\alpha^2 mc^2 = \frac{e^2}{a_0}). \tag{16.17}$$

In particular, for the ground-state energy this approximation gives

$$E = 2E_1 = -\tfrac{1}{2}\alpha^2 mc^2 \cdot 2Z^2 = -108.8 \text{ eV} \qquad (Z = 2),$$

which is eight times the energy of the H ground state, therefore the He ground state is very deep (this will not change qualitatively with subsequent corrections). The first excited state corresponds to $n_1 = 1, n_2 = 2$ and gives

$$E' = E_1 + E_2 = -\tfrac{1}{2}\alpha^2 mc^2 \cdot \tfrac{5}{4} Z^2 = -68.0 \text{ eV},$$

while the energy of the excited state with $n_1 = n_2 = 2$ is

$$E'' = 2E_2 = -\tfrac{1}{2}\alpha^2 mc^2 \cdot \tfrac{1}{2} Z^2 = -27.2 \text{ eV}.$$

The ionization energy of He is obtained as the difference between the energy of the He^+ ion (the free electron is considered to be at rest) and the energy of the ground state, that is,

$$I = E_1 - 2E_1 = -E_1 = \tfrac{1}{2}\alpha^2 mc^2 Z^2 = 54.4 \text{ eV}. \tag{16.18}$$

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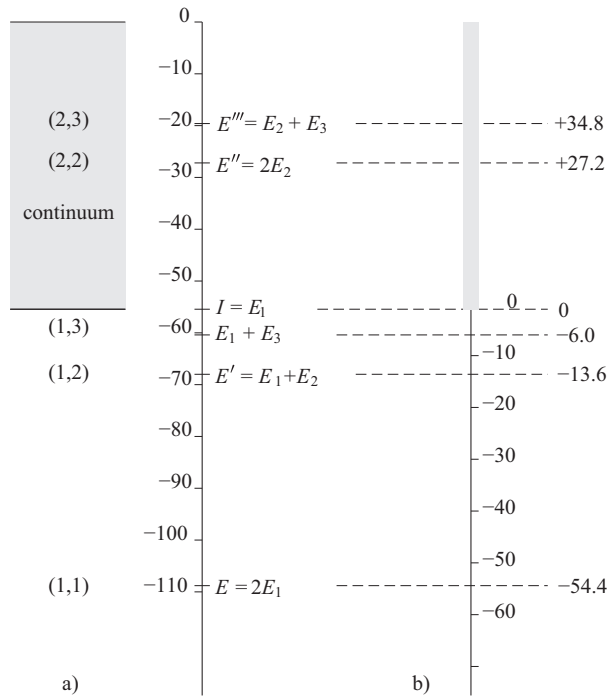


Figure 16.1 Spectrum of a helium-like atom, neglecting the Coulomb repulsion between the electrons. In (a) the energy scale corresponds to the case where the energy of the infinitely excited state ($n_1, n_2 \to \infty$) is zero. In (b) the zero of the energy is set at the continuum threshold; the ground-state energy is then equal to $-I$, and for positive energies the atom ionizes.

These results are shown in Fig. 16.1(a). When an energy $\geq I$ is supplied to an atom in its ground state, one of its electrons is released; the released electron can have any energy, so the new system (ion + emitted electron) is in the continuum. As usual, we fix the origin of the energy at the threshold of the continuum, that is, at 54.4 eV above the ground-state energy (as in Fig. 16.1(b)). Note that an interesting phenomenon occurs: atoms with two outer electrons (and, in particular, the helium-like atom) have excited states such as $(2s)^2$ which are in the continuum (positive energies). The excited states of interest are therefore reduced to those with one $1s$ electron and the other in the nl orbital ($n \neq 1$), which have the continuum as their asymptotic limit.

The fact that all the other excited states are in the continuum gives rise to characteristic effects, such as the Meitner–Auger or self-ionization effect (discovered by Lise Meitner[6] in 1922 and by Auger[7] shortly afterwards), which consists in the fact that, once one such state is produced (e.g., by absorption of radiation), the system can decay without emitting radiation into a He^+ ion and an emitted electron. From now on, we will limit the study of the He spectrum to the discrete states, so we will assume that one

[6] Lise Meitner (1878–1968) was an Austrian-born physicist whose influential work forced her to flee Germany for Sweden in 1938, where she discovered the power of the nuclear fission reaction.

[7] Pierre Auger (1899–1993) was a French physicist who worked in the fields of atomic, nuclear, and cosmic-ray physics.

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of the electrons is in the $1s$ state. Since the other electron is in one of the $|nlm\rangle$ states, we can use its quantum numbers to characterize the state of the atom and write the energy in the form E_{nl} (this energy must also depend on the total electronic spin, 0 or 1, as we will see later). With this notation, Eq. (16.17) becomes

$$E_{nl} \simeq -\tfrac{1}{2}\alpha^2 mc^2 \left(Z^2 + \frac{Z^2}{n^2}\right). \tag{16.19}$$

It is possible to improve this expression (at least for large values of n and l) without having to go deeper into the calculation, by the following considerations. If n and l are large enough, the nl orbital will be concentrated in regions much further away from the nucleus than the inner $1s$ orbital. Therefore, while the entire nuclear charge Z acts on the inner electron, only the charge $Z - 1$ acts on the outer electron. Consequently, instead of (16.19) we write

$$E_{nl} \simeq -\tfrac{1}{2}\alpha^2 mc^2 \left(Z^2 + \frac{(Z-1)^2}{n^2}\right), \tag{16.20}$$

expressing the shielding effect of the nucleus by the electron. The result of a variational calculation confirms the soundness of this consideration, as we will see later.

16.3.1 Perturbative solution

To improve the calculation of the He spectrum, we will first use a perturbative method. The choice of the unperturbed Hamiltonian is not trivial and depends largely on the purpose of the calculation. If we are interested in simplicity rather than precision, the obvious choice is to consider the potential between the electrons as the perturbation, as was done before; the minimum-energy state then corresponds to $(1s)^2$. For the total wave function to be antisymmetric, the spinor factor must be antisymmetric; the system is therefore in the state $S = 0$ (antiparallel spins). The first-order correction to the ground-state energy is then given by

$$\delta E_{10}^{(1)} = \int d^3r_1 d^3r_2 \Psi_{10}^*(\boldsymbol{r}_1, \boldsymbol{r}_2) \frac{e^2}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} \Psi_{10}(\boldsymbol{r}_1, \boldsymbol{r}_2), \tag{16.21}$$

where

$$\Psi_{10}(\boldsymbol{r}_1, \mathbf{r}_2) = \psi_{100}(\boldsymbol{r}_1)\psi_{100}(\boldsymbol{r}_2)\chi_0, \tag{16.22}$$

with χ_0 the spinor wave function, which in obvious notation takes the form

$$\chi_0 = \frac{1}{\sqrt{2}}\left[\chi_+(1)\chi_-(2) - \chi_-(1)\chi_+(2)\right]. \tag{16.23}$$

Since the interaction does not contain spin operators, and $|\chi_0|^2 = 1$, the energy correction reduces to

$$\delta E_{10}^{(1)} = e^2 \int |\psi_{100}(\boldsymbol{r}_1)|^2 \frac{1}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} |\psi_{100}(\boldsymbol{r}_2)|^2 d^3r_1 d^3r_2. \tag{16.24}$$

Inserting here the hydrogen-like ground-state functions and rearranging, we get

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$$\delta E_{10}^{(1)} = \frac{e^2 Z^6}{\pi^2 a_0^6} \int_0^\infty r_1^2 e^{-2Zr_1/a_0} dr_1 \int_0^\infty r_2^2 e^{-2Zr_2/a_0} dr_2 \times \int_{\Omega_1} d\Omega_1 \int_{\Omega_2} d\Omega_2 \frac{1}{(r_1^2 + r_2^2 - 2r_1 r_2 \cos\theta)^{1/2}}, \tag{16.25}$$

where θ is the angle formed by $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$. Aligning the z axis in the direction of $\boldsymbol{r}_1$, we have (with $x = \cos\theta$)

$$\int d\Omega_1 \int \frac{d\Omega_2}{|\boldsymbol{r}_1 - \mathbf{r}_2|} = 4\pi \int_0^{2\pi} d\varphi \int_{-1}^{1} \frac{dx}{(r_1^2 + r_2^2 - 2r_1 r_2 x)^{1/2}} = \frac{4\pi^2}{r_1 r_2}(r_1 + r_2 - |\boldsymbol{r}_1 - \boldsymbol{r}_2|), \tag{16.26}$$

whence

$$\delta E_{10}^{(1)} = \frac{8e^2 Z^6}{a_0^6} \int_0^\infty r_1^2 e^{-2Zr_1/a_0} \times \left[\frac{1}{r_1} \int_0^{r_1} r_2^2 e^{-2Zr_1/a_0} dr_2 + \int_{r_1}^\infty r_2 e^{-2Zr_2/a_0} dr_2 \right] dr_1. \tag{16.27}$$

This result can be obtained directly if we remember that the electrostatic potential outside an isotropic charge distribution is equal to that produced by a point charge at the center of the distribution, while inside the distribution it is constant and equal to that of the surface. Carrying out the radial integrals, we obtain

$$\delta E_{10}^{(1)} = \tfrac{5}{4} Z \cdot \tfrac{1}{2} \alpha^2 mc^2, \tag{16.28}$$

so that the ground-state energy is to first order

$$E_{10}^{(1)} = -\tfrac{1}{2} \alpha^2 mc^2 (2Z^2 - \tfrac{5}{4} Z). \tag{16.29}$$

This gives for the He atom

$$E_{10}^{(1)} = -74.8 \text{ eV}, \tag{16.30}$$

which differs from the experimental value $E_{10}^{\text{exp}} = -78.97$ eV by 5–6%. The result is stimulating, considering the crudeness of the calculation. A higher-order perturbative calculation is extremely tedious, so a variational method is used instead for a better estimate.

To estimate the variational corrections to the energy of the excited states, we must first construct the zero-order wave functions. Since one electron is in the $1s$ state and the other in the nl state with $n \neq 1$, the orbital wave function must be the symmetric combination of ψ_{100} and ψ_{nlm} if $S = 0$, and the antisymmetric one if $S = 1$, where S represents the total spin of the two orbital electrons. Therefore we write

$$\Psi_{nl}^{\pm} = \psi_{\pm}(\boldsymbol{r}_1, \boldsymbol{r}_2) \chi_S, \tag{16.31}$$

where

$$\psi_{\pm} = \tfrac{1}{\sqrt{2}} [\psi_{100}(\boldsymbol{r}_1)\psi_{nlm}(\boldsymbol{r}_2) \pm \psi_{100}(\boldsymbol{r}_2)\psi_{nlm}(\boldsymbol{r}_1)] \tag{16.32}$$

(the + sign corresponds to $S = 0$ and the − sign, to $S = 1$). From here (and even from (16.22)) we see that the He wave function describes in each case an entangled state,

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with all its consequences.[8] Moreover, these states are described as waves in a six-dimensional configuration space. It is clear that if ψ is taken as a probability amplitude, the dimensionality of space does not in principle pose a problem; but the peculiarities associated with entanglement remain.

The first-order energy correction can be written in the form

$$\delta E_{nl}^{(1)} = J_{nl} \pm K_{nl}, \tag{16.33}$$

where J_{nl} and K_{nl} are given by

$$J_{nl} = e^2 \int |\psi_{100}(\boldsymbol{r}_1)|^2 \frac{1}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} |\psi_{nlm}(\boldsymbol{r}_2)|^2 d^3 r_1 d^3 r_2, \tag{16.34}$$

$$K_{nl} = e^2 \int \psi_{100}^*(\boldsymbol{r}_1)\psi_{nlm}^*(\boldsymbol{r}_2) \frac{1}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} \psi_{100}(\boldsymbol{r}_2)\psi_{nlm}(\boldsymbol{r}_1) d^3 r_1 d^3 r_2. \tag{16.35}$$

Both integrals can be calculated in closed form (the calculation is laborious and will not be done here) and are positive (this is obvious for J).

16.3.2 Orthohelium and parahelium

According to Eq. (16.33), the energy spectrum will depend on the total spin state. The states with $S = 0, 1$ correspond to parahelium and orthohelium respectively. As seen in Fig. 16.2, the orthohelium states lie below the corresponding parahelium states; this is a particular example of the empirical Hund rule mentioned earlier. We can understand this by noting that in the orthohelium the parallel electronic spins tend to repel each other, so the average distance between the electrons is greater than in the parahelium; this reduces the electrostatic repulsion between them and lowers their energy relative to the parahelium states. It can be shown that the transition $l = 0 \to l = 0$ is strictly forbidden for all orders of multipole moments, so both the $1s2s$ state of the parahelium and the $2s$ state of the orthohelium are metastable. Here we have a concrete example of a system whose ground state (the 1s2s of orthohelium) has nodes, since the surface $\boldsymbol{r}_1 = \boldsymbol{r}_2$ is a nodal surface (this possibility was mentioned in Section 15.3).

The existence of orthohelium and parahelium is a manifestation of exchange effects, that is, of how purely electrostatic interactions give rise to effects that can be described in terms of spin (which results in a somewhat artificial description), due to the fact that the spatial distribution of the particles is conditioned by the spin coupling.

To give the exchange effects a more concrete physical meaning, we will describe how the electrons periodically exchange roles when their energies are comparable. To do this, we take as the general orbital solution to first order in perturbation theory the function

$$\Psi(t) = a_+ \psi_+(t) + a_- \psi_-(t), \tag{16.36}$$

where

$$\psi_\pm(t) = \psi_\pm(\boldsymbol{r}_1, \boldsymbol{r}_2) e^{-i\omega_\pm t}. \tag{16.37}$$

[8] See the discussion in Section 14.5.

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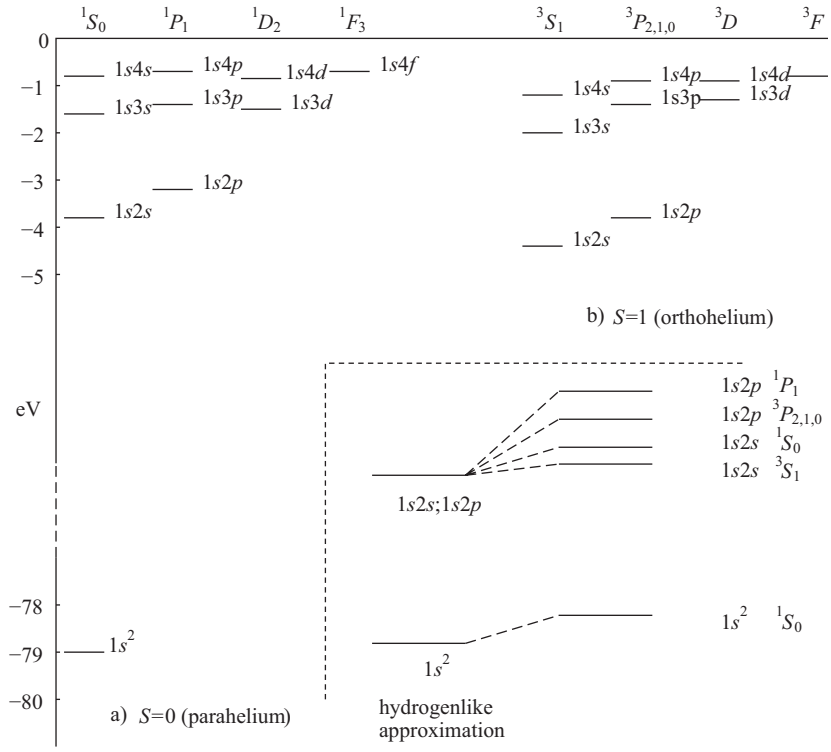


Figure 16.2 He energy levels. Parahelium (a) and orthohelium (b) energy spectra are shown schematically, indicating both the electronic configuration and the atomic state. The insert shows how the hydrogen-like levels separate due to exchange. Because of spin–orbit coupling and other corrections, levels like $^3P_{2,1,0}$ are not really degenerate.

The perturbed energies $\hbar\omega_\pm$ are given to first order by

$$\omega_\pm \equiv \omega \pm \delta\omega \equiv \frac{E_{nl}^{(0)} + J_{nl} \pm K_{nl}}{\hbar}. \tag{16.38}$$

To examine the time behavior of Ψ, let us take $a_+ = a_- = 1/\sqrt{2}$. At $t = 0$, $\Psi(0) = \psi_{10}(1)\psi_{nl}(2)$ describes the situation in which (statistically speaking) the electrons 1 are in the $1s$ state and the electrons 2 are in the nl state. At a later time t, we have

$$\Psi(t) = e^{-i\omega t}\left[\psi_{10}(1)\psi_{nl}(2)\cos\delta\omega\, t - i\,\psi_{10}(2)\psi_{nl}(1)\sin\delta\omega\, t\right]. \tag{16.39}$$

Therefore, at the time t_1 given by

$$t_1 = \frac{\pi}{2\delta\omega} = \frac{\pi\hbar}{2K_{nl}}, \tag{16.40}$$

we have $\Psi(t) = -ie^{-i\omega t_1}\psi_{10}(2)\psi_{nl}(1)$, which describes the situation where the electrons 2 are in the $1s$ state and the electrons 1 are in the nl state. that is, the electrons have exchanged their roles. The exchange time t_1 is determined by K_{nl}; the larger this integral (i.e., the greater the overlap between the functions ψ_{10} and ψ_{nl}), the more frequent the exchange. If $K_{nl} = 0$, each electron remains in its state without exchanging energy

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($t_1 = \infty$); in this case we are dealing with two essentially independent systems. Intuitively, if one electron is in a highly excited state and therefore very far from the nucleus, and the other is in the inner $1s$ state, the interaction between the electrons is so small that no significant exchange can be expected.[9]

To get a more quantitative idea of this exchange phenomenon, we take $n = 2$ and $l = 0$, and proceed as we did to evaluate the integral in (16.25), which yields

$$K_{20} \simeq \left(\frac{4}{27}\right)^2 \frac{Ze^2}{a_0}, \tag{16.41}$$

whence from Eq. (16.40), ($\alpha = e^2/\hbar c \sim 1/137$ is the fine-structure constant)

$$t_1 \simeq \left(\frac{3}{2}\right)^6 \frac{\pi a_0}{\alpha c} \sim 10^{-15}\text{s}. \tag{16.42}$$

Since αc is of the order of the electron's orbital velocity and πa_0 is of the order of the length of the orbit, t_1 is of the order of the electron's rotation period; this indicates that the relatively large overlap between ψ_{10} and ψ_{20} causes the electrons to switch roles at almost every rotation. However, with $n = 10$, $l = 0$, t_1 spans years; in this case each electron remains in its state without interfering with the other, and the orbital solution is essentially reduced to the product $\psi_{10}(1)\psi_{nl}(2)$ ($n \gg 1$).

16.3.3 Variational solution

To demonstrate the possibilities of the variational method for the study of atomic systems, we will apply it to the case of the helium-like atom in its ground state. As a simple test function, it is customary to use the expressions (16.22) and (13.148), but treating the coefficient in the exponential as a variational parameter,

$$\psi_{10} = \frac{1}{\pi}\left(\frac{A}{a_0}\right)^3 \exp\left[-\frac{A}{a_0}(r_1 + r_2)\right] \tag{16.43}$$

(we have omitted the spin factor). This choice is equivalent to not fixing the value of Z beforehand, or replacing $Z = 2$ by another value Z^* corresponding to the partially shielded nuclear charge, which is determined variationally. This idea was used in writing (16.20), with $Z^* = Z$ for the inner electron and $Z^* = Z - 1$ for the outer one. If, as we propose with the choice (16.43) for the test function, the value of Z^* must be common to both electrons, we can anticipate that it will be close to $Z - \frac{1}{2}$.

The expectation value of the Hamiltonian (16.16) calculated with the test function (16.43) is

$$\langle \widehat{H} \rangle = \frac{e^2}{a_0}\left[A^2 - (2Z - 5/8)A\right] = -\alpha^2 mc^2 A(2Z - 5/8 - A). \tag{16.44}$$

[9] Atoms with one or more highly excited electrons (where the level n can be even higher than 100) are called *Rydberg atoms*, and they have several peculiar properties, including long decay times, large electric dipole moments, and wave functions that approximate classical orbits; the outermost (valence) electrons are subject to a potential similar to that of an H atom. Rydberg atoms are currently the subject of intense research because of their many applications, including radio-frequency sensing, quantum optics, quantum computing, quantum simulation, and astrophysics. For example, Rydberg spectral lines have been detected corresponding to H atoms and C atoms several microns in diameter.

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Table 16.3 Ionization energy of some atoms.

Ion	Experiment	Variational method One parameter	Many parameters
He	0.90372	0.85	0.90369
Li^{+}	2.7799	2.72	2.77991
Be^{+++}	5.656	5.50	5.65556
C^{++++}	14.41	14.35	14.4063

Minimizing this expression with respect to A gives $A = Z - 5/16$, whence

$$E_{10} \leq \min\langle \widehat{H} \rangle = -\alpha^2 mc^2 \left(Z - \tfrac{5}{16}\right)^2, \tag{16.45}$$

that is, the effective nuclear charge is $Z^* = Z - 5/16$, confirming our prediction. For $Z = 2$ this gives $E_{10} < -77.4$ eV, which is within 2% of the experimental result -78.97 eV.

What is measured in the laboratory is not the energy E_{10}, but the ionization potential, which, as we have seen, is given by $I = E_0 - E_{10}$, where E_0 represents the energy of the hydrogen-like ion. It is customary to express the results in atomic units (au), in which $e^2/a_0 = \alpha^2 mc^2 = 1$ (i.e., $e = m = \hbar = 1$ and $c = 1/\alpha \approx 137$). With this convention, we obtain for the energy

$$E_{10} = -\left(Z - \tfrac{5}{16}\right)^2 = -2.85 \text{ au} \quad \text{for } Z = 2, \tag{16.46}$$

and for the ionization potential

$$I = \left(Z - \tfrac{5}{16}\right)^2 - \tfrac{1}{2}Z^2 = \tfrac{1}{2}\left(Z^2 - \tfrac{5}{4}Z + \tfrac{25}{128}\right) = 0.85 \text{ au} \quad \text{for } Z = 2; \tag{16.47}$$

the current experimental value is 0.9036 au. Variational calculations with several tens of parameters give results that differ from experiment by less than 10^{-6} au. Table 16.3 shows the results obtained with the variational method for other ions ("many parameters" refers to calculations made with up to 50 parameters).

It is useful to compare the result (16.46) with those obtained using the Hartree and Hartree–Fock methods, which were originally used precisely to study the ground state of He. With the Hartree method, a product wave function of two orbitals gives $E_{10} = -2.862$ au, while the introduction of the Pauli principle reduces this value to $E_{10} = -2.876$ au, which differs from the experimental value (-2.903 au) by less than 1%. The main advantage of Hartree's method applied to helium-like atoms is that it gives the most accurate wave functions in the form of a product of two orbitals, whereas the variational method gives a better result for the ionization potential.

Exercise E16.1. Magnetic properties of parahelium
Determine the magnetic properties of parahelium in its ground state.

Solution. The ground state of parahelium has zero total angular momentum, so it is a diamagnetic gas. The diamagnetic properties are conveniently described in terms of the magnetic susceptibility, given by the Langevin formula Eq. (14.48),

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$$\chi_{\text{diam}} = -\frac{e^2 N}{6mc^2}\langle r_1^2 + r_2^2\rangle. \tag{16.48}$$

Since the atom is in its ground state, to calculate the required expectation values we can use as the wave function the one provided by the variational method, Eq.(16.43), using the previously determined value for A, $A = Z^* = 27/16$. This gives

$$\langle r_1^2 + r_2^2\rangle = \frac{2a_0^2}{Z^{*2}}, \tag{16.49}$$

so that the diamagnetic susceptibility per gram atom is

$$\chi_{\text{diam}} = -\frac{e^2 N a_0^2}{3mc^2 Z^{*2}} \simeq -1.67 \times 10^{-6}. \tag{16.50}$$

This result compares favorably with the experimental value $\chi_{\text{exp}} = -1.9 \times 10^{-6}$.

16.4 Molecular Structure

16.4.1 Nature of the chemical bond

In Section 16.1 we saw that in simple compounds (e.g., inorganic salts) the valence with which each of the elements intervenes is determined by the number of electrons that each one of the atoms gives up (positive ionic valence) or gains (negative ionic valence). However, this picture of the chemical bond as the result of electrostatic attraction between two ions, or between an ion and a neutral atom polarized by the presence of the ion, is not sufficient to explain the vast majority of chemical bonds. In particular, it cannot explain the existence of structures as simple as the homonuclear diatomic molecules H_2, O_2 or N_2. In such cases we speak of covalent or homopolar bonds, and the valence responsible for them is called spin valence.

We seem to be faced with the need to construct two different theories of chemical bonding, involving two types of atomic valence. In reality, however, a single notion of valence suffices, and we can speak of a generic type of chemical bond, the extreme cases of which, namely purely ionic or purely covalent bonds, are never realized in the strict sense. In order to prepare the ground for a more general discussion of this important topic, which is at the basis of theoretical chemistry, we will first study the simplest of all molecules, the H_2 molecule and its ion, H_2^+.

16.4.2 The molecular hydrogen ion H_2^+

The existence of the H_2^+ on indicates that the electrostatic attraction exerted simultaneously by the electron on the two nuclei can be sufficient to overcome the electrostatic repulsion between them: the orbital electron is the molecular cement.

To understand qualitatively how a H_2^+ molecule is formed, suppose that a neutral H atom (in its ground state) and a proton (which can be thought of as an H^+ atom)

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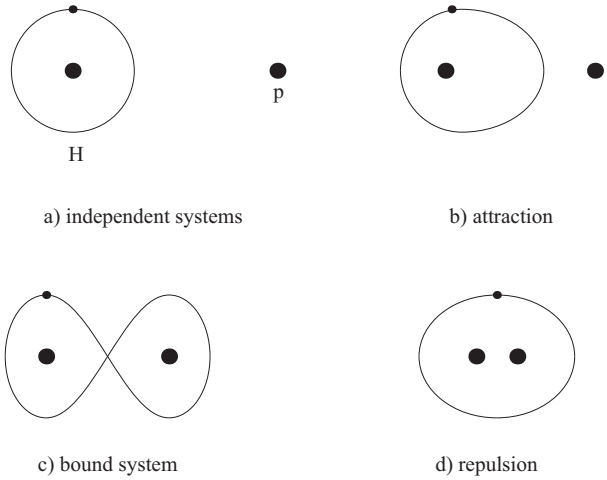


Figure 16.3 The effects of a proton approaching a neutral H atom are shown schematically. The polarization induced by the proton leads to an initial attraction between the atoms until a stable molecule is formed. At very small distances beyond which a common orbit is established, the repulsion between the nuclei becomes the dominant force.

approach each other from a great distance. As a result, the electron orbit is deformed by the attraction between the proton and the electron, as shown schematically in Fig. 16.3. If the two subsystems are close enough, the strong attraction of the proton to the electron can cause a situation similar to that shown in Fig. 16.3(c), where the electron is trapped by both nuclei, following a complicated orbit.[10]

As we will see later, under these conditions the system remains bound. As the nuclei come closer together, as in Fig. 16.3(d), the electron no longer travels in between the nuclei, and the internuclear repulsion exceeds the weak attraction of the electron. As a result, the protons tend to separate until they return to a situation like the previous one, where the average attractive and repulsive forces are in balance.

Suppose that the H_2^+ molecule has been formed and is in a stationary state, as shown in Fig. 16.3(c). Roughly speaking, we can say that the orbital electron spends half its time in the state $\psi_A(\boldsymbol{r})$ around nucleus A and the rest of its time in the same state, but around nucleus B, which we denote by $\psi_B(\mathbf{r})$. This crude *statistical* description of the molecule is represented by the wave function

$$\Psi(\boldsymbol{r}) = N[\psi_A(\boldsymbol{r}) + \psi_B(\boldsymbol{r})]\chi. \tag{16.51}$$

Wave functions such as this, constructed using a linear combination of atomic orbitals, are called molecular orbitals, and this method of describing the molecular state is known as the LCAO method (where the abbreviation stands for linear combination of atomic orbitals).

[10] The illustrations in Fig. 16.3 are conventional and do not imply that each electron follows a smooth orbit, but only that there is an orbital motion, probably very complicated and random, which can be represented on average by a smooth and periodic closed curve, like the one shown in the illustration.

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16.4.3 The H_2 molecule

The previous observations serve as a guide to describing the H_2 molecule. To simplify the task, we will assume that in the CM system the two nuclei are at rest; their relative motion can be introduced later as a perturbation (see Section 16.6). So we simply write the product of the molecular orbitals (MO) of the two electrons, which is equivalent to neglecting the interaction between them. We also need to introduce the spinor wave function χ and a normalization factor N,

$$\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = N[\psi_A(\boldsymbol{r}_1) + \psi_B(\boldsymbol{r}_1)][\psi_A(\boldsymbol{r}_2) + \psi_B(\boldsymbol{r}_2)]\chi_0. \tag{16.52}$$

This wave function describes a situation where each electron is close enough to one of the nuclei for a part of the time and the motion of the two electrons is essentially independent.

We have explicitly written the spin factor χ_0 corresponding to the total electron spin $S = 0$ because the orbital factor in (16.52) is invariant under the exchange of electrons, so the spin factor must be antisymmetric for the total wave function to be antisymmetric. This is a special case of a general empirical rule which states that the ground state of the molecules of virtually all chemically stable compounds of elements of the main groups has zero spin; notable exceptions are O_2 ($S = 1$), and NO, NO_2, ClO_2 ($S = 1/2$). However, since we are not considering spin–orbit coupling, the choice of a particular spin factor is practically irrelevant. Later we will have the opportunity to verify that the proposed choice (antisymmetric spinor wave function) is the correct one.

For the treatment of H_2^+ the wave function (16.51) is the only one allowed to zero order. However, for molecules with more than one valence electron, including H_2, an alternative method of constructing the wave function to zero order (i.e., neglecting the interactions between the valence electrons and between the nuclei) can be used. This method, called mesomerism or valence bonding, introduced by Heitler[11] and London[12] in 1927, considers the molecule as a structure made up of atoms. We can easily explain the idea using the example of H_2. Half the time electron 1 is bound to nucleus A, in the atomic orbital $\psi_A(1)$, while the other electron is bound to nucleus B, in the atomic orbital $\psi_B(2)$; this composite state is described by $\psi_I = \psi_A(1)\,\psi_B(2)$. The rest of the time, the electrons will have swapped roles (not their energies) and the state will be described by $\psi_{II} = \psi_B(1)\psi_A(2)$. Therefore, the wave function that describes the molecule statistically for all times can be approximated by[13]

$$\Psi(1,2) = N(\psi_I + \psi_{II})\chi_0 = N[\psi_A(1)\psi_B(2) + \psi_B(1)\psi_A(2)]\chi_0, \tag{16.53}$$

where N is the normalization constant (which varies from case to case). Each of the two terms in this expression is a valence orbital.

[11] Walter Heinrich Heitler (1904–1981) was a German physicist, best known for his contributions to quantum electrodynamics.

[12] Fritz Wolfgang London (1900–1954) was a German-born physicist who made fundamental contributions to the theories of chemical bonding and of intermolecular forces. He was unsuccessfully nominated several times for the Nobel Prize in Chemistry.

[13] We have once again restricted ourselves to symmetric orbitals and antisymmetric spinors. In this case we have an additional argument in favor of this choice, namely that the antisymmetric orbital combination has a nodal surface at $\mathbf{r}_1 = \mathbf{r}_2$, so that it does not belong to the ground state, which is the one we are examining.

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The two preceding descriptions are approximate, in that they both neglect all interactions except those that bind the electrons. Both take into account, in different ways, the basic effect of the proximity of the atoms, that is, the fact that each valence electron "belongs" half the time to one nucleus. Because of the different way in which the exchange is introduced, these methods are not equivalent in detail, but they give numerical results that are as accurate as if a sufficiently large number (several tens) of variational parameters were used. To illustrate the difference between the two methods, we expand the MO wave function Eq. (16.52),

$$\Psi(1,2) = N_1[\psi_A(1)\psi_A(2) + \psi_B(1)\psi_B(2)]\chi_0 + N_2[\psi_A(1)\psi_B(2) + \psi_B(1)\psi_A(2)]\chi_0. \tag{16.54}$$

The first term describes two complementary situations: (a) the two electrons are bound to nucleus A and nucleus B has none; (b) the two electrons are bound to B and nucleus A has none. In both cases there is a negative ion (a proton with two orbital electrons) and a positive one (a bare proton); these represent (purely) ionic bonds. The second term on the right is precisely the Heitler–London wave function and represents the (purely) covalent coupling, that is, the sharing of the electron pair between the two atoms. In the case of the H_2 molecule, ionic bonding (the first term) is almost nonexistent, so the wave function (16.53) gives a better description than (16.52) when N_1 and N_2 are taken as equal; but the opposite happens if both parameters are determined variationally. In most cases, it is precisely a combination of ionic and covalent binding, such as Eq. (16.54), that correctly describes the physical situation. Since the LCAO method (with free coefficients) allows both types of bonds to be generated simultaneously, it is widely used in the theoretical study of molecules, usually in combination with the self-consistent field method.

16.4.4 Energy calculations for H_2^+ and H_2

We now carry out the explicit calculations, based on the preceding discussion. To simplify the procedure, we will first consider the H_2^+ ion and take the adiabatic approximation, in which the nuclear motion is neglected. The Hamiltonian of the system is

$$\widehat{H} = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{|\boldsymbol{r} - \boldsymbol{r}_A|} - \frac{e^2}{|\boldsymbol{r} - \boldsymbol{r}_B|} + \frac{e^2}{|\boldsymbol{r}_A - \boldsymbol{r}_B|}, \tag{16.55}$$

where $\boldsymbol{r}_A, \boldsymbol{r}_B, \boldsymbol{r}$ represent the position of the two nuclei and of the electron respectively. With nucleus A at the origin of coordinates and nucleus B at the position $\boldsymbol{R}$, the Hamiltonian takes the form

$$\widehat{H} = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{r} - \frac{e^2}{|\boldsymbol{r} + \boldsymbol{R}|} + \frac{e^2}{R}. \tag{16.56}$$

Although the Schrödinger equation with this Hamiltonian is solvable in elliptic coordinates, we will take a more elementary approach by applying the variational method

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with a single free parameter (Wang, 1928). As a test function we take the one given by Eq. (16.51) with

$$\psi_A(\boldsymbol{r}) = \left(\frac{1}{\pi a_0^3}\right)^{1/2} e^{-r/a_0}, \tag{16.57}$$

and similarly for B. To be more general, we will examine the predictions obtained not only with the function (16.51), but also with the one with the antisymmetric orbital factor. So instead of (16.51) we write

$$\Psi_\pm(\boldsymbol{r}, \boldsymbol{R}) = N_\pm[\psi_A(\boldsymbol{r}, \boldsymbol{R}) \pm \psi_B(\boldsymbol{r}, \boldsymbol{R})]\chi, \tag{16.58}$$

with the normalization factor given by

$$N_\pm = \langle A \pm B | A \pm B \rangle^{-1/2} \equiv [2 \pm 2S(R)]^{-1/2}, \tag{16.59}$$

where S depends on the internuclear distance, which plays the role of the variational parameter and must be selected so that the energy of the system is a minimum. Specifically, S measures the overlap between A and B,

$$S(R) = \langle A | B \rangle \tag{16.60}$$

and its value is

$$S = \frac{1}{\pi a_0^3} \int \exp\left[-\frac{|\boldsymbol{R} - \boldsymbol{r}|}{a_0} - \frac{r}{a_0}\right] d^3r. \tag{16.61}$$

The calculation of the energy of H_2^+ and H_2 requires the solution of several integrals of this type or more complicated ones. Starting from the formula

$$\frac{e^{-kr}}{r} = \frac{1}{2\pi^2} \int \frac{e^{i\boldsymbol{q}\cdot\boldsymbol{r}}}{q^2 + k^2} d^3q, \tag{16.62}$$

the validity of which should be checked by direct evaluation, and differentiating (16.54) with respect to k, one gets

$$e^{-kr} = \frac{k}{\pi^2} \int \frac{e^{i\boldsymbol{q}\cdot\boldsymbol{r}}}{(q^2 + k^2)^2} d^3q, \tag{16.63}$$

which can be used to write the hydrogen-like wave function as an integral over q,

$$\psi_A(\mathbf{r}) = \left(\frac{1}{\pi a_0}\right)^{5/2} \int \frac{e^{i\boldsymbol{q}\cdot\boldsymbol{r}}}{(q^2 + 1/a_0^2)^2} d^3q. \tag{16.64}$$

Equation (16.61) becomes thus

$$\begin{aligned} S &= \left(\frac{1}{\pi a_0}\right)^5 \int \frac{e^{i\boldsymbol{q}\cdot\boldsymbol{r}}}{(q^2 + 1/a_0^2)^2} \cdot \frac{e^{i\boldsymbol{q}'\cdot(\boldsymbol{R}-\boldsymbol{r})}}{(q'^2 + 1/a_0^2)^2} d^3q\, d^3q'\, d^3r \\ &= \frac{8}{\pi^2 a_0^5} \int \frac{e^{i\boldsymbol{q}'\cdot\boldsymbol{R}}\delta(\boldsymbol{q} - \boldsymbol{q}')}{(q^2 + 1/a_0^2)^2 (q'^2 + 1/a_0^2)^2} d^3q\, d^3q' \\ &= \frac{8}{\pi^2 a_0^5} \int \frac{e^{i\boldsymbol{q}\cdot\boldsymbol{R}}}{(q^2 + 1/a_0^2)^4} d^3q. \end{aligned} \tag{16.65}$$

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To obtain this result, we first integrated over $\boldsymbol{r}$; the integral over $\boldsymbol{q}$ is carried out as usual, taking the z axis in the direction of $\boldsymbol{R}$,

$$S = \left[1 + \frac{R}{a_0} + \frac{1}{3}\left(\frac{R}{a_0}\right)^2\right] e^{-R/a_0}. \tag{16.66}$$

For integrals involving the Coulomb potential we can use Eq. (16.62); thus, for example,

$$\frac{1}{|\boldsymbol{R} - \boldsymbol{r}|} = \frac{1}{2\pi^2} \int \frac{e^{i\boldsymbol{q}\cdot(\boldsymbol{R}-\boldsymbol{r})}}{q^2} d^3q. \tag{16.67}$$

With this we conclude our mathematical digression and return to the central theme. The expectation value of the Hamiltonian (16.56) is (with $\langle A|\widehat{H}|A\rangle = \langle B|\widehat{H}|B\rangle$ and $\langle A|\widehat{H}|B\rangle = \langle B|\widehat{H}|A\rangle$),

$$\begin{aligned}\langle \widehat{H}\rangle &= N_\pm^2 \langle A \pm B|\widehat{H}|A \pm B\rangle \\ &= \frac{1}{1 \pm S}[\langle A|\widehat{H}|A\rangle \pm \langle A|\widehat{H}|B\rangle].\end{aligned} \tag{16.68}$$

Using E_1 to denote the ground-state energy of the H atom, we write

$$\begin{aligned}\langle A|\widehat{H}|A\rangle &= \langle A|\left(-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{r}\right) + \frac{e^2}{R} - \frac{e^2}{|\boldsymbol{R} + \boldsymbol{r}|}|A\rangle \\ &= E_1 + \frac{e^2}{R} - e^2\langle A|\frac{1}{|\boldsymbol{R} + \boldsymbol{r}|}|A\rangle \\ &= E_1 + e^2\left(1 + \frac{R}{a_0}\right)\frac{\exp(-2R/a_0)}{R}.\end{aligned} \tag{16.69}$$

Likewise,

$$\begin{aligned}\langle A|\widehat{H}|B\rangle &= \left(E_1 + \frac{e^2}{R}\right) S - e^2\langle A|\frac{1}{|\boldsymbol{R} + \boldsymbol{r}|}|B\rangle \\ &= \left(E_1 + \frac{e^2}{R}\right) S - \frac{e^2}{a_0}\left(1 + \frac{R}{a_0}\right)\exp(-R/a_0).\end{aligned} \tag{16.70}$$

Substituting these values and the value of S from (16.66), we obtain with $x \equiv R/a_0$,

$$\langle \widehat{H}\rangle = E_1 + \frac{e^2}{R}\frac{(1+x)e^{-2x} \pm (1 - 2x^2/3)e^{-x}}{1 \pm S}. \tag{16.71}$$

This result is characteristic: the chemical forces decrease exponentially with the internuclear distance. As expected, the energy is reduced to that of an H atom as the distance between the nuclei increases indefinitely. The energy of the system has as its upper bound the minimum of (16.71),

$$E \leq \min\langle \widehat{H}\rangle. \tag{16.72}$$

The complexity of the expression for $\langle \widehat{H}\rangle$ makes it preferable to use numerical methods to determine the value of x that minimizes it. The results for the symmetric (+) and antisymmetric (−) selections of the wave function (16.58) are shown in Fig. 16.4. We note that for the antisymmetric solution there is no minimum for the energy at finite internuclear distances and that this exceeds E_1 for all R, so that the minimum energy

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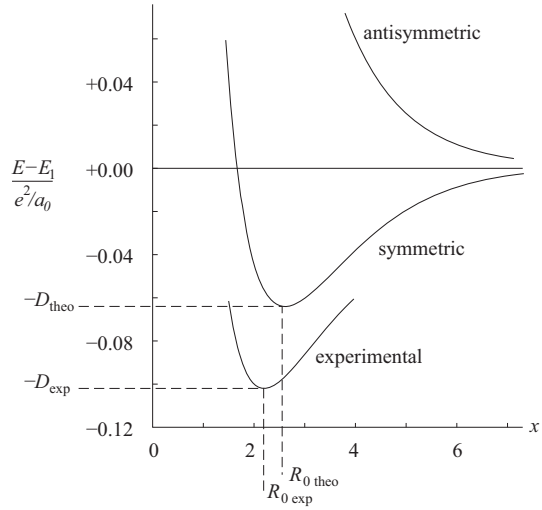


Figure 16.4 Curves showing the energy of the H_2^+ molecule (in units of e^2/a^2) as function of the internuclear distance.

state corresponds to infinitely separated nuclei, that is, it is a repulsive state. The symmetric solution, on the other hand, has a minimum with an energy lower than that of the H atom, so the formation of the molecule is energetically advantageous and the system binds. The equilibrium distance read from the curve is $R_0 = 5a_0/2$, which is about 1.2 Å. The binding energy of the molecule is then (D is the dissociation energy, i.e., the work required to separate the molecule into its constituent atoms)

$$E_{\text{bind}} \equiv -D = E_{\text{min}} - E_1 = -0.065\frac{e^2}{a_0} = 0.13E_1 = -1.76\,\text{eV}. \tag{16.73}$$

The corresponding experimental values are 1.06 Å and $D = 2.79\,\text{eV}$, as can be seen in Fig. 16.4. Qualitatively, the results are very satisfactory, since the theory explains the formation of the molecule; quantitatively, they are poor, since the discrepancy between theoretical and experimental values is considerable. However, when multiple parameters are introduced, the variational method accurately predicts the experimental results.

The H_2 molecule can be treated in the same way. In this case the Hamiltonian is

$$\widehat{H} = \frac{\widehat{p}_1^2}{2m} + \frac{\widehat{p}_2^2}{2m} - \frac{e^2}{r_{1A}} - \frac{e^2}{r_{1B}} - \frac{e^2}{r_{2A}} - \frac{e^2}{r_{2B}} + \frac{e^2}{r_{12}} + \frac{e^2}{R}, \tag{16.74}$$

where the notation is that given in Fig. 16.5. The wave function should be taken with its orbital part symmetric according to the results with the H_2^+ ion, and can be chosen in the form of (16.52) (a product of molecular orbitals) or (16.53) (a sum of valence orbitals). In both cases the electrons are in a singlet state. With the MO method, the expectation value of the Hamiltonian becomes

$$\langle\widehat{H}\rangle = 2E_{\text{H}^+}(R) - \frac{e^2}{R} + \langle\frac{e^2}{r_{12}}\rangle. \tag{16.75}$$

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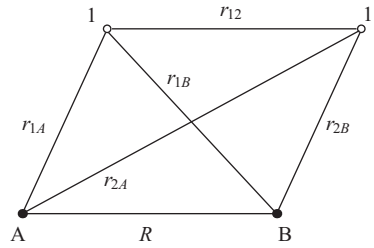


Figure 16.5 Coordinates of the particles that make up an H_2 molecule.

The explicit form of the electron repulsion term is relatively complicated and will not be given here. What is important is that this expression is qualitatively analogous to that obtained for the H_2^+ ion; the numerical analysis fixes $R = 0.85\,\text{Å}$ as the equilibrium distance, which corresponds to the binding energy $E = -2.68\,\text{eV}$. The experimental values are $0.74\,\text{Å}$ and $-4.74\,\text{eV}$, so the agreement between this approximation and the experiment is only qualitatively satisfactory. Using the Heitler–London method, that is, the wave function (16.53), the final results obtained are $R = 0.80\,\text{Å}$ and $E = -3.14\,\text{eV}$, which do not represent a significant improvement. In both cases many variational parameters are required to obtain a reasonably accurate description. We conclude that the introduction of the second electron only changes the details, as long as the two electrons forming the covalent bond have antiparallel (paired) spins.

16.4.5 Valence bonds

If a third H atom approaches an H_2 molecule, they will repel each other regardless of the direction of their spins, that is, the H_3 molecule will not form. In such cases, the valence of the molecule is said to be saturated, so that it cannot form any further bonds. This phenomenon does not occur at the classical level because classically no force is saturated. For example, the Sun can gravitationally attract any body that approaches it, regardless of how many are already in its gravitational field.

Valence saturation, a common quantum phenomenon, explains why there are no molecules like H_3 or why noble gases are chemically inert. It can be understood by considering that the valence electrons of an atom are the unpaired outer electrons. If an atom has n of these electrons, its maximum spin is $S_{\max} = n/2$; therefore the valence of a configuration is twice the maximum possible spin of that configuration (this does not apply to transition elements, which may have specific properties). For example, nitrogen in its ground state has the configuration $1s^2 2s^2 2p^3$ and spin 3/2; the $1s$ and $2s$ electrons are paired, and there are three p electrons with parallel spin, so the valence is 3 (see Fig. 16.6). However, the weakly excited state with the same electron configuration but two paired $2p$ electrons, shown in Fig. 16.6, has spin 1/2; in this configuration N is monovalent. We see that valence is a property of the state of the system and can be multiple for a given element. Therefore, the chemical properties of an atom are fundamentally determined by the maximum spin valence of its lowest states. We will analyze the elements of the periodic table on this basis.

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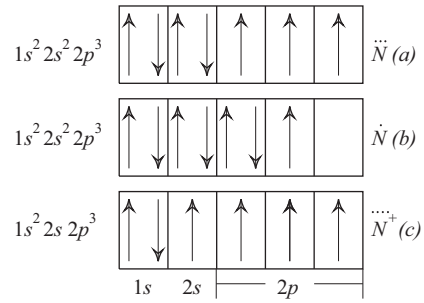


Figure 16.6 In the external configuration $2s^2 2p^3$, N has valence 3 in its ground state (quadruplet) and 1 in the excited state (doublet). In configuration $2s2p^3$ its valence is 5 (4 spin and 1 ionic).

As can be seen from Tables 16.1 and 16.2, the elements of Group I (which includes the six alkali metals Li, Na, K, Rb, Cs and Fr) have only one outer electron, which is necessarily unpaired ($S = 1/2$), so their valence is 1. The spin can only increase when an electron leaves a closed shell, producing highly excited states that do not form stable molecules; hence all these elements are exclusively monovalent.

Group II elements (Be, Mg, Ca, Sr, Ba, Ra) have two outer paired s-electrons ($S = 0$) in their ground state, so their valence is 0 and they do not form compounds in this state. However, they have a slightly excited state in which one s-electron goes to the p state, changing the s^2 configuration to sp; in this case the electrons are unpaired ($S = 1$) and the valence is 2.

A similar situation occurs with the elements of group III (containing the first group of transition metals Bo, Al, etc.), which in their ground state have the $s^2 p$ outer configuration with $S = 1/2$ and a valence of 1; however, the slightly excited sp^2 configuration corresponds to a valence of 3, so that these elements (with the exception of B and Al) are mono- and trivalent.

The elements of group IV have the outer configuration $s^2 p^2$ ($S = 1$) in the ground state and the slightly excited configuration sp^3 ($S = 2$), so they have valences of 2 and 4; however, C normally has only the valence 4 (except in the compound CO), a fact on which organic chemistry is based. Similarly, the elements of groups V and VI have the valences 1, 3, 5 and 0, 2, 4, 6 respectively.

The atoms of group VII (which includes the halogens) have the external configuration $s^2 p^5$ in their ground state with $S = 1/2$, so they are monovalent, although through their excited configurations they can have the additional valences 3, 5, 7 (with the exception of F, which is exclusively monovalent). For example, chlorine acts with valence 1, 3, 5, 7 in the compounds HCl, $HClO_2$, $HClO_3$ and $HClO_4$, respectively.

The elements of group 0 (noble gases; it now contains the element 118 oganesson, the heaviest element of the table so far) have the outer configuration s^2 ($S = 0$); again, since spin can only be obtained by extracting a closed-shell electron, a process that requires too much energy, the only valence they have is 0, which explains the chemical inactivity of these gases, and the name of the group.

The transition elements can act with valences that differ by 1 and not only by 2, as is the case with the main group elements; this can occur, for example, by the transition of f electrons to s or p states. The noble metals (Cu, Ag, Au, Pl) have similar properties to

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those of the transition metals. For example, Cu has a $4s$ electron that is easily released, giving it alkali-metal properties. However, it has slightly excited states in which a $3d$ electron goes to the $4s$ or $4p$ subshell, where it tends to lose two electrons to form the cupric ion; in these compounds the d subshell is incomplete and the metal tends to behave as befits a transition element.

So far it has not been necessary to distinguish between the homopolar and the heteropolar nature of the bond; the difference between them is purely quantitative, and in practice any intermediate case can occur. There are, of course, situations where the nature of the bond is clearly defined. For example, in the third case shown in Fig. 16.6 the N atom will have lost an s electron, producing an ionic valence which, when added to the four spin valences of the $2s2p^3$ outer configuration, gives this configuration the valence 5 characteristic of group V elements.

16.4.6 Valence bonding and chemical forces

The above discussion allows us to understand some other properties of chemical forces in a simple way. For example, once two valence electrons from different atoms form a bond (and pair up in a singlet), they become chemically inactive, leading to saturation. Another consequence of the scheme is that a molecule will normally have zero spin. However, there are also unsaturated covalent bonds, formed between two atoms by the overlap of half-filled valence atomic orbitals of each atom containing an unpaired electron. Their appearance can be explained using the example of the simplest metal, Li: its electronic configuration is $1s^2 2s$, so its outer shell is analogous to that of H and it forms the molecule Li_2. However, it happens that the $1s^2 2p$ configuration has almost the same energy, which makes this molecule radically different from H_2, whose first excited state is very high. If we now bring a third Li atom close to the Li_2 molecule, a bond is formed with the electron in the $2p$ atomic orbital, allowing the exclusion principle to be reversed in this case. In fact, this process can be repeated many times, as there are a large number of atomic orbitals of virtually the same energy. It is these unsaturated bonds that give rise to metallic crystals in which each atom is bonded to its neighbors, sharing each valence electron with several of them. In particular, this is what allows extra charges (extra electrons) to move very easily from atom to atom, giving metals their characteristic electrical properties.

It is an experimental fact that molecules have a well-defined spatial structure. For example, the H_2O molecule is triangular, the CO_2 molecule is linear, the NH_3 molecule is pyramidal, etc. The quantum theory of valence allows us to explain these structures using the concept of directed valence associated with p orbitals. Let us take N as an example to illustrate the idea. The three valence p electrons can be described by three linearly independent orbitals, denoted p_x, p_y, and p_z, whose angular wave functions are given by

$$\langle \theta, \varphi | p_x \rangle = \frac{1}{\sqrt{2}} \left(-Y_1^1 + Y_1^{-1} \right) = \sqrt{\frac{3}{4\pi}} \sin\theta \cos\varphi, \tag{16.76}$$

$$\langle \theta, \varphi | p_y \rangle = i \frac{1}{\sqrt{2}} \left(Y_1^1 + Y_1^{-1} \right) = \sqrt{\frac{3}{4\pi}} \sin\theta \sin\varphi, \tag{16.77}$$

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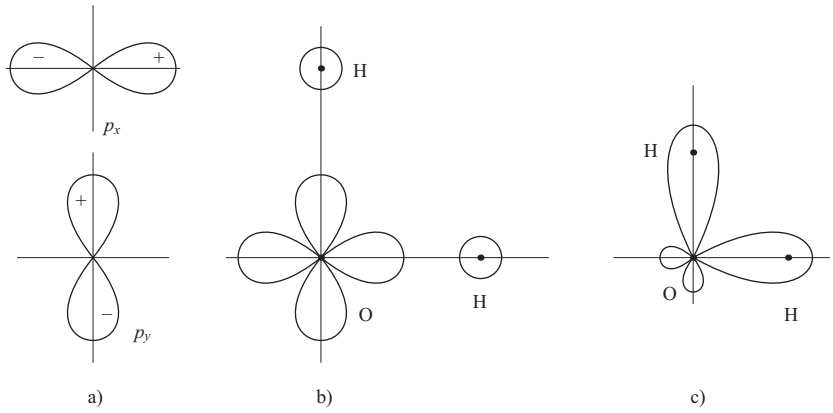


Figure 16.7 The water molecule. In (a) the p_x and p_y atomic orbitals of O are shown schematically; in (b) the O and H atomic orbitals are shown when they are far apart (the overlap is zero). At distances where the overlap is significant, the atomic orbitals combine as shown in (c) to form the molecular orbitals. In the resulting water molecule, the two H atoms are not at 90° to each other; the repulsion between them increases this angle to 104.45°.

$$\langle \theta, \varphi | p_z \rangle = Y_1^0 = \sqrt{\frac{3}{4\pi}} \cos\theta. \tag{16.78}$$

The directions in which the electron density has a maximum when its spatial distribution is given by these functions are mutually orthogonal. It follows that the directions of the three bonds formed by the valence electrons will be orthogonal, since the overlap with the electrons of atoms approaching in these directions will be maximum. In particular, the NH_3 molecule should then have a pyramidal structure with the three H atoms at the base and the N atom at the apex, and an angle of 90° between the three NH bonds. Experiment shows that this angle is 107.3°; the difference is explained by the electrostatic repulsion between the H atoms, which allows the N atom to move closer to the base of the pyramid.

The principle of maximum overlap used in the previous explanation is at the basis of all stereochemistry. Take the water molecule as a second example. The two outer 2p electrons of O are in orthogonal orbitals, such as p_x and p_y, so the H bonds will be maximal along these directions, as shown in Fig. 16.7. If the effect of the 2*s* electrons on the molecule is taken into account by using as orbitals not the *p* states, but linear orthogonal combinations of *s* and *p* states, so as to minimize the energy of the bonded system (a procedure called hybridization of atomic orbitals, proposed by Pauling), it turns out that the hybridized orbitals form an angle of 109.6° with each other. The remaining discrepancy with the experiment (104.45°) is due to the fact that the 2*s* electrons are not fully equivalent to the 2*p* electrons because of their lower energy, which implies partial hybridization. The hybridization procedure is essential to explain, for example, why the four valences of carbon are entirely equivalent, even though the configuration that produces them is $2s2p^3$: the *s* electron and the 3 *p* electrons form four sp^3 hybrid orbitals in a highly symmetric tetragonal structure, with a bond angle of 109.6°. This is precisely the structure of methane, CH_4.

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Due to the great difficulty of the subject, there is still no satisfactory theory of the covalent bonding of complex molecules, and it is sometimes necessary to limit oneself to qualitative considerations. On the other hand, in order to describe these systems, the quantum laws must be supplemented with additional elements that take into account the influence of the specific properties of the compounds under consideration.

Exercise E16.2. Angular momentum selection rules for diatomic molecules
Based on qualitative considerations, discuss the selection rules for rotational angular momentum of homonuclear diatomic molecules.

Solution. The eigenfunctions of the Hamiltonian are symmetric or antisymmetric with respect to the geometric center of the molecule, so the electron density is symmetric; consequently a homonuclear molecule does not have an electric dipole moment. It follows from this that there are no electric dipole transitions in these molecules, so the basic radiation spectrum is produced by magnetic dipole or electric quadrupole transitions, whose selection rules for L are $\Delta L = 0, \pm 1, \pm 2$. However, it is possible to eliminate the rule $\Delta L = \pm 1$ from the following considerations. The symmetry of the total molecular wave function, including the nuclear spins, is defined by the rules of maximum symmetrization; since the spins are not affected during molecular transitions (spin–orbit and spin–spin couplings are negligible), the symmetry of the orbital function cannot change, which requires that the parity of L be preserved, that is, radiative transitions can only involve even changes in L. Then $\Delta L = 0, \pm 2$ are the requested selection rules.

16.5 Effects of Nuclear Motion on Diatomic Molecules

To analyze the effects of the nuclear motion on molecular spectra, we write the Schrödinger equation for a diatomic molecule in the form

$$[\widehat{T}_r + \widehat{T}_R + V(\boldsymbol{r}, \boldsymbol{R})]\Psi(\boldsymbol{r}, \boldsymbol{R}) = E\Psi(\boldsymbol{r}, \boldsymbol{R}), \tag{16.79}$$

where $\widehat{T}_r$ is the total kinetic energy of the electrons, $\widehat{T}_R$ that of the nuclei, and $V(\boldsymbol{r}, \boldsymbol{R})$ the total potential energy, which includes the repulsions between nuclei, the attractions between them and the electrons, and the repulsions between the latter; all other effects are neglected. A perturbative treatment of the problem can be made by considering the nuclei fixed (all $\boldsymbol{R}$s constant), so that the Schrödinger equation reduces to

$$[\widehat{T}_r + V(\boldsymbol{r}, \boldsymbol{R})]\psi_n = \mathcal{E}_n(\boldsymbol{R})\psi_n, \tag{16.80}$$

where $\mathcal{E}_n(\boldsymbol{R})$ is the total electronic energy. The approximation method introduced by Born and Oppenheimer[14] in 1927 starts by using the solutions of Eq. (16.80) to expand the solutions of (16.79) in the form

[14] Julius Robert Oppenheimer (1904–1967) was a US-born theoretical physicist who made significant contributions to quantum mechanics and nuclear physics. Recruited to work on the Manhattan Project during World War II, he later campaigned against the nuclear arms race.

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$$\Psi(\boldsymbol{r}, \boldsymbol{R}) = \sum_m \varphi_m(\boldsymbol{R})\psi_m(\boldsymbol{r}, \boldsymbol{R}). \tag{16.81}$$

After some simplifications one obtains

$$\sum_m [\widehat{T}_R\varphi_m\psi_m + \mathcal{E}_m(\boldsymbol{R})\varphi_m\psi_m] = E\sum_m \varphi_m\psi_m. \tag{16.82}$$

Since

$$\widehat{T}_R\varphi_m(\boldsymbol{R})\psi_m(\boldsymbol{r}, \boldsymbol{R}) = \psi_m\widehat{T}_R\varphi_m + \varphi_m\widehat{T}_R\psi_m - \frac{\hbar^2}{M}(\nabla_R\varphi_m)\cdot(\nabla_R\psi_m), \tag{16.83}$$

where M is the reduced nuclear mass (half the mass of each nucleus for a homonuclear molecule), and in the region close to equilibrium the electronic functions ψ vary slowly with R (see Figure 16.4), Eq. (16.82) reduces to

$$\sum_m \psi_m[\widehat{T}_R\varphi_m + \mathcal{E}_m(R)\varphi_m] = E\sum_m \psi_m\varphi_m. \tag{16.84}$$

Multiplying by $\psi_n^\dagger$ and integrating over all electronic variables, one gets a Schrödinger equation for the nuclear motion,

$$\widehat{T}_R\varphi_n + \mathcal{E}_n(R)\varphi_n = E\varphi_n, \tag{16.85}$$

which shows that the electronic energy $\mathcal{E}_n(R)$ of the state under consideration is the potential that determines the nuclear motion. This potential has a shape similar to that shown in Figure 16.4, and its dependence on the parameter R is very complicated. For this reason, the study of nuclear motion with Eq. (16.85) is done by approximating $\mathcal{E}_n(R)$ with a reasonably constructed function that reproduces its basic properties and is mathematically simple at the same time. A well-known approximation is the Morse[15] potential (1929),

$$\mathcal{E}(R) = -D + D\left[e^{-(R-R_0)/a} - 1\right]^2, \tag{16.86}$$

where D represents the dissociation energy and R_0 is the equilibrium distance at which the potential is a minimum, $\mathcal{E}'(R_0) = 0$. The Morse potential gives good results for reasonable deviations from R_0 but cannot be used to study the behavior of the system for very large R, where the interaction potential decreases as R^{-6} instead of exponentially, as explained in Section 16.6.1.

In a diatomic molecule, the relative motion of the nuclei occurs around R_0 as long as it is not in a highly excited vibrational state. The potential can then be expanded in a Taylor series around R_0. From (16.86) to second order it follows that

$$\mathcal{E}_n(R) = -D + \tfrac{1}{2}M\omega_0^2(R - R_0)^2, \tag{16.87}$$

with

$$D = -\mathcal{E}_n(R_0), \tag{16.88}$$

$$M\omega_0^2 = \left(\frac{\partial^2\mathcal{E}_n}{\partial R^2}\right)_{R=R_0}, \tag{16.89}$$

[15] Philip McCord Morse (1903–1985) was a US-born theoretical physicist who pioneered operations research. He wrote several outstanding physic texts, among which Morse and Feshbach (1953) stands out, having been the bible of theoretical physics for many decades.

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so that from (16.85) one gets

$$\frac{\hbar^2}{2M}\nabla^2\varphi + [E + D - \tfrac{1}{2}M\omega_0^2(R - R_0)^2]\varphi = 0. \tag{16.90}$$

The nuclear motion has thus been separated into two independent components: a rigid-body rotation (studied in Section 12.3), and oscillations about the equilibrium distance with the characteristic frequency ω_0 given by Eq. (16.89). Since the potential is central, we can immediately write the radial equation for the function $u(R) = R\varphi(R)$,

$$\frac{d^2u}{dR^2} + \frac{2M}{\hbar^2}\left[E + D - \frac{1}{2}M\omega_0^2(R - R_0)^2 - \frac{\hbar^2 L(L+1)}{2MR^2}\right]u = 0, \tag{16.91}$$

where L is the angular momentum of the rigid rotation of the molecule. It is convenient to pass from R to $r = R - R_0$; in the centrifugal term we can take $R^{-2} = (R_0 + r)^{-2} \simeq R_0^{-2}$, so that (16.91) reduces to the equation for a harmonic oscillator,

$$\frac{d^2u}{dr^2} + \frac{2M}{\hbar^2}\left[E + D - \frac{\hbar^2 L(L+1)}{2MR_0^2} - \frac{1}{2}M\omega_0^2 r^2\right]u = 0. \tag{16.92}$$

The total energy is then

$$E = -D + \hbar\omega_0\left(K + \tfrac{1}{2}\right) + B\hbar L(L+1), \quad (K = 0, 1, 2, \dots) \tag{16.93}$$

with

$$B = \frac{\hbar}{2MR_0^2} = \frac{\hbar}{2I}. \tag{16.94}$$

The molecule dissociates when $E > 0$; this means that it has a finite number of discrete energy levels, those that satisfy the inequality

$$\hbar\omega_0\left(K + \tfrac{1}{2}\right) + B\hbar L(L+1) \geq D. \tag{16.95}$$

Physically, this limitation results from the fact that if the molecule rotates with very high angular momentum, the centrifugal force overcomes the binding forces, or if the vibrational energy is too high ($K \gg 1$), the atoms move too far apart.

From Eq. (16.93) we see that the energy of the molecule can be expressed as the sum of an electronic, a vibrational and a rotational contribution,

$$E = E_{\text{elect}} + E_{\text{vib}} + E_{\text{rot}}, \tag{16.96}$$

with

$$E_{\text{rot}} \ll E_{\text{vib}} \ll |E_{\text{elect}}| = D. \tag{16.97}$$

To confirm these inequalities, we proceed as follows. Let a be a characteristic dimension of the molecule; the kinetic energy of the electrons is at least of the order of that required by Heisenberg's inequality, $p^2/2m \sim \hbar^2/2ma^2$. Hence

$$|E_{\text{elect}}| \sim \frac{\hbar^2}{ma^2}. \tag{16.98}$$

With this estimate we can write $\partial^2\mathcal{E}/\partial R^2 \sim \hbar^2/ma^4$, whence from (16.89),

$$E_{\text{vib}} \sim \hbar\omega_0 \sim \sqrt{\frac{m}{M}}|E_{\text{elect}}|. \tag{16.99}$$

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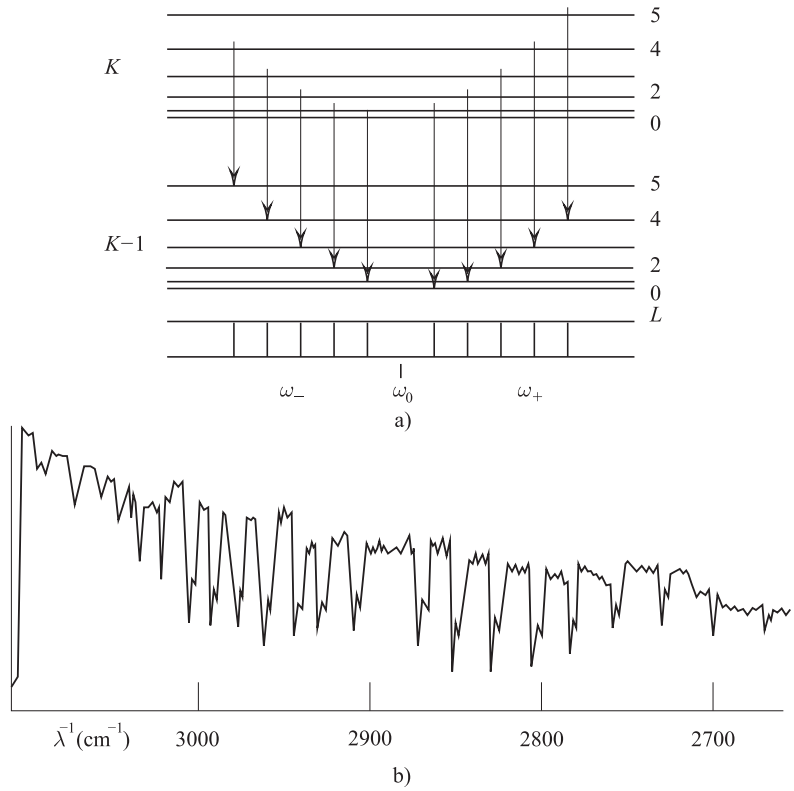


Figure 16.8 Vibrational–rotational spectrum of a diatomic molecule. In (a) the basic structure of the spectrum is shown as a succession of equidistant lines, in which the line corresponding to the frequency ω_0 is missing, since the transition $\Delta l = 0$ is forbidden. In (b) an absorption curve of electromagnetic radiation by HCl molecules is shown (the abscissa corresponds to $\lambda^{-1} = \omega/2\pi c$), with no line of frequency ω_0. The double peaks in the minima are due to the presence of two Cl isotopes.

Finally, we have

$$E_{\text{rot}} \sim \frac{\hbar^2}{Ma^2} = \frac{m}{M}\frac{\hbar^2}{ma^2} = \frac{m}{M}|E_{\text{elect}}|. \tag{16.100}$$

The vibrational-rotational emission spectrum results from the fact that during transitions the vibrational quantum number K must decrease (by 1), but L can increase ($L \to L+1$) or decrease ($L \to L-1$), since the system is deenergized anyway due to the lost vibrational energy; hence the radiated frequencies are

$$\omega^{\pm} = \frac{E(K,L) - E(K-1, L\pm 1)}{\hbar} = \omega_0 + \begin{cases} -2B(L+1) \\ +2BL \end{cases} \tag{16.101}$$

as shown in Fig. 16.8(a). Experimental analysis of this spectrum (in molecules such as CO, HCl, etc.) allows the determination of important molecular properties, such as moments of inertia, the isotopic composition of the nuclei, and so on.

A diatomic molecule can have a spectrum in the visible range that is much more complicated than those we have derived, consisting of more or less broad bands (band

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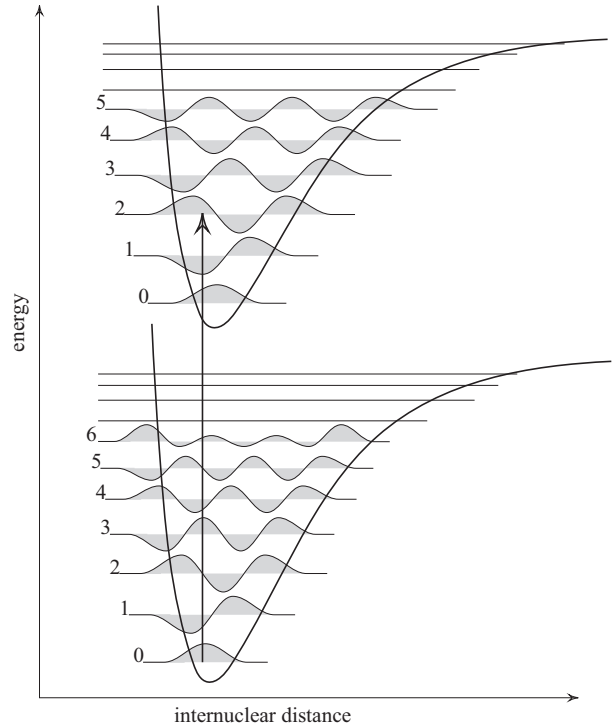


Figure 16.9 In a diatomic molecule the potential energy curves for the lower and upper electronic states are different. According to the Franck–Condon principle, the transitions are "vertical," that is, the nuclei do not move while the electrons are excited; note that the electronic transition is accompanied by a change in the vibrational quantum number.

spectrum), often formed by a large number of very close lines that start abruptly at a certain point. The treatment of this problem is greatly simplified by the introduction of the Franck–Condon principle. This principle states that, due to the large difference between the nuclear and electronic masses, the nuclei practically do not move while an electronic transition takes place (Fig. 16.9). Once a transition has taken place, the binding forces change and so does the internuclear distance, which modifies the molecule's moment of inertia; this change can excite vibrational and rotational states by energy exchange. As a result, the frequencies of the spectral lines become

$$\omega = \omega_1 + \omega_{LL'}, \tag{16.102}$$

with

$$\omega_1 = \frac{E_n - E_{n'}}{\hbar} \pm \omega_0, \tag{16.103}$$

$$\omega_{LL'} = BL(L+1) - B'L'(L'+1). \tag{16.104}$$

This gives rise to three independent branches, with frequencies

$$\omega^+ = \omega_1 + \omega_{LL-1} = \omega_1 + (B - B')L^2 + (B + B')L, \tag{16.105}$$

$$\omega^0 = \omega_1 + \omega_{LL} = \omega_1 + (B - B')L(L+1), \tag{16.106}$$

$$\omega^- = \omega_1 + \omega_{LL+1} = \omega_1 + (B - B')(L+1)^2 - (B + B')(L+1). \tag{16.107}$$

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Exercise E16.3. The specific heat of a diatomic gas

Based on the results just presented, discuss the behavior of the specific heat of diatomic gases as a function of temperature.

Solution. Each molecule of a diatomic gas has 6 degrees of freedom: 3 translational, 2 rotational, and 1 vibrational. In the classical limit (at high temperatures) each degree of freedom contributes to the specific heat per molecule with the amount $\frac{1}{2}k$ (k is the Boltzmann constant), so the specific heat per molecule is given by $c_V = 3k$. However, when the average energy $\frac{3}{2}kT$ associated with the translational motion of the molecule is less than the energy difference between two adjacent vibrational levels, the collisions between molecules due to thermal agitation cannot excite the vibrational modes. The molecule then behaves like a rigid body with only 5 degrees of freedom; that is, the vibrations are frozen and the specific heat is only $\frac{5}{2}k$. The temperature at which the vibrational modes thaw is

$$\tfrac{3}{2}kT_{\text{vib}} = \hbar\omega. \tag{16.108}$$

Substituting into this expression the value of the vibrational frequency of H_2, we find that $T_{\text{vib}} \sim 10^3 K$, whereas for Cl_2 the vibrations contribute already at room temperature . These results ($c_V = \frac{5}{2}k$ and $3k$, respectively) are in agreement with the experiment (Fig. 16.10).

Similarly, we can define a threshold (defrost) temperature for the rotations using the equation

$$\tfrac{3}{2}kT_{\text{rot}} = \frac{\hbar^2}{2I}. \tag{16.109}$$

For any temperature below T_{rot} the diatomic molecule will behave with only 3 (translational) degrees of freedom, that is, as monatomic with specific heat $\frac{3}{2}k$. For hydrogen, for example, $T_{\text{rot}} \sim 50K$. Furthermore, taking into account that at low temperatures the statistics of the system are quantum and not classical, we have to use the quantum theory of specific heats, which predicts that c_V tends to zero with temperature, as seen in Section 2.3.2. The general character of the specific heat per molecule for a diatomic

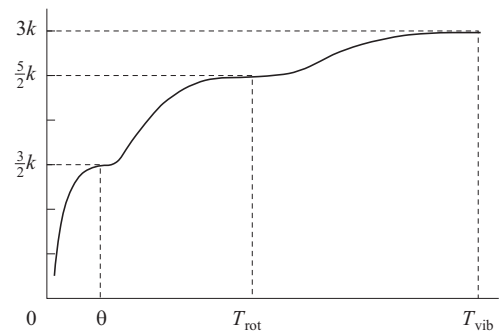


Figure 16.10 Specific heat of a diatomic gas as a function of temperature. The Debye temperature θ is a property of the material (more rigid materials have a higher θ).

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gas is summarized in Figure 16.10, where θ (the Debye temperature) is a characteristic parameter of the gas.

16.6 Intermolecular Forces. Casimir and van der Waals Forces, Measurable Effects of the ZPF

Intermolecular forces are much weaker than the intramolecular forces of attraction, but they play a central role in determining the physical properties of aggregates of molecules, such as their boiling point, melting point, density, and enthalpies of fusion and evaporation,[16] and are also responsible for most of the chemical properties of matter.

In order from strongest to weakest, intermolecular forces can exist between an ion and a dipole (this is why, for example, some ionic compounds dissolve in water); H bonding (between the hydrogen attached to an electronegative atom in a molecule, such as O, N, or F, and another electronegative atom); between permanent dipoles, or between induced dipoles.

When two molecules come very close together, so that their electron clouds overlap, electrostatic forces arise between them, such as those associated with the chemical bonds. These chemical forces, which occur when the centers of the molecules are separated by 3 A or less, tend to be attractive and decrease rapidly (exponentially) with increase in distance; they are therefore considered to be short-range.

At long distances, on the other hand, there are attractive forces between molecules, generated by the coupling of their dipoles or multipoles, whose potential energy decreases with intermolecular distance, usually as R^{-6} or faster. Because of their relatively long range, these forces are critical in determining the properties of real gases and of some liquids and solids, including surface tension, friction, viscosity, vapor pressure, evaporation, and solubility. More generally, intermolecular forces play a crucial role in physics, chemistry, and biology; without intermolecular forces there would be virtually no solids or liquids; no nanostructures, biological molecules, or cellular structures could form.

Dipole–dipole interactions occur between polar molecules.[17] These forces arise from the alignment of the permanent or induced dipoles, enhancing the intensity of the attractive interactions. Polar molecules, such as water and ammonia, have an uneven distribution of electrons, resulting in positive and negative ends. The positive end of one molecule is attracted to the negative end of another, forming a weak electrostatic interaction.

Hydrogen bonding, a subset of dipole–dipole interactions, involves a particularly strong type of molecular attraction. It occurs when H atoms from one molecule form strong bonds with highly electronegative atoms, such as N, O, or F, in neighboring

[16] An enthalpy is a thermodynamic quantity equal to the total heat content of the system, i.e., the sum of its internal energy and the product pV.

[17] A polar molecule has the effective structure of an electric dipole due to the accumulation of charge on one side, and of the opposite charge in the other side.

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molecules. The presence of H bonding is responsible for various extraordinary properties of water, including its high boiling point, density anomaly, and surface tension. It also plays a vital role in the structures and functions of biomolecules such as DNA and proteins.

16.6.1 Van der Waals forces

Van der Waals interactions are ubiquitous, existing between atoms, molecules, colloidal particles, and macroscopic objects. Van der Waals[18] forces include various types of attractive and repulsive long-range interatomic or intermolecular forces, resulting from *transient* shifts in electron density. Unlike ionic or covalent bonds, these attractions do not arise from a chemical electronic bond; they arise from the interaction between uncharged atoms or molecules, are comparatively weak, and vanish at larger distances between molecules. They lead not only to phenomena such as the cohesion of condensed phases, the physical absorption of gases and the self-assembly of nanomaterials, but also to a universal force of attraction between macroscopic bodies.

A molecule with a permanent dipole can *induce* a dipole in a similar neighboring molecule and cause mutual (induced dipole–dipole) attraction. This interaction is called the *Debye force*, named after P. Debye. A simple example is the interaction between the HCl molecule and the noble gas Ar. In this system, the Ar atom becomes a dipole as its electrons are attracted to the H side of HCl or repelled from the Cl side. The angle-averaged HCl–Ar interaction is given by the equation

$$V = \frac{-d_1^2 \alpha_2}{16\pi^2 \varepsilon_0^2 \varepsilon_r^2 R^6}, \tag{16.110}$$

where α_2 is the polarizability of the atom. This force is much weaker than a dipole–dipole interaction, but stronger than the London dispersion force.

The most important van der Waals forces are the *dispersion forces*,[19] the basic theory of which was formulated by London et al. (1926–1930). The London dispersion forces arise from attractive interactions between the *instantaneously induced* dipoles of molecules. Polarization can be induced either by a polar molecule or by the repulsion of negatively charged electron clouds in non-polar molecules. They are the weakest intermolecular forces, and yet they produce important phenomena, such as the tendency of colloidal particles to aggregate, which in turn may be the basis for other effects, such as coagulation, and so on. They are the most important component of the van der Waals forces because all materials are polarizable, whereas the Debye forces require permanent dipoles. The term dispersion forces derives from their association with optical dispersion.

The dispersion forces are traditionally considered to be purely quantum, that is, not explainable by classical physics. From the usual quantum point of view, two neutral polarizable bodies attract each other because the quantum fluctuations of one of them induce a dipole moment in the other, which in turn induces a dipole moment in the first

[18] Johannes van der Waals (1837–1923) was a Dutch theoretical physicist, famous for his pioneering work on the equation of state for real gases, for which he was awarded the Nobel Physics Prize in 1910.
[19] The term dispersion refers to the relation between energy and momentum.

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one. The distance dependence of these dispersion forces can be estimated by noting that the dipole field of the first particle falls off as R^{-3} so that the strength of the induced dipole has this dependence, and the interaction energy of two dipoles also varies as R^{-3}, giving an overall R^{-6} dependence.

Exercise E16.4. Attractive van der Waals force between a neutral atom and a conducting plate

Calculate the interaction energy between a neutral atom and a perfectly conducting flat plate as a function of the distance, considering the interaction potential between the atom and its image.

Solution. Let d be the distance between the atom and the plate. If the plate is on the xy-plane, the interaction potential between the atom and its image is obtained from Eq. (16.115) by setting $e_2 = -e_1 = -e$, $x_2 = x_1 = x$, $y_2 = y_1 = y$, $z_2 = -z_1 = z$, $R = 2d$. Therefore,

$$\mathcal{H} = -\frac{e^2}{8d^3}(x^2 + y^2 + 2z^2). \tag{16.111}$$

For an H atom in its ground state, the first-order interaction energy from perturbation theory is

$$\mathcal{E} = \langle 100|\mathcal{H}|100\rangle = -\frac{e^2}{8d^3}4a_0^2 = E_1\left(\frac{a_0}{d}\right)^3, \tag{16.112}$$

where E_1 is the energy of the ground state. We see that the force with which the wall attracts the neutral atom is proportional to $1/d^4$ and is due to the dipole interaction with the image itself. Note that for the interaction between two independent dipoles it is required to use second-order perturbation theory, since $\langle 0|x_i|0\rangle = 0$, which produces a potential $\sim 1/d^6$; however, for dipole–plate the first-order theory suffices, which generates the much stronger interaction $\sim 1/d^3$.

16.6.1.1 Van der Waals force between two H atoms

The theoretical study of intermolecular forces is best carried out using the variational method introduced in Section 13.8. To keep things simple, we will consider the long-distance interaction between two H atoms; the generalization to the case of molecules is straightforward in principle, but can become very complex in practice.

Because of the large distance between the two atoms, we do not need to consider exchange effects (the Pauli principle applies in this case to each atom separately, whereas, if the overlap were important, it would apply to the system as a whole).[20] If $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$ represent the position coordinates of the electrons with

[20] There is no rigorous formulation of the conditions under which the Pauli principle ceases to apply (or, more generally, when exchange effects cease to be important). Intuitively, if the wave functions of the constituents of the physical system have a significant overlap, the system forms a unit and the Pauli principle should apply (for coupled systems this happens at small distances, or on the order of the dimensions of the smaller of the constituents). On the other hand, if the overlap is negligible (e.g., at large distances), we can consider the parts to be (essentially) independent, and the Pauli principle applies to each of them separately.

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respect to their own nucleus and $\boldsymbol{R}$ is the vector connecting them, we can write the Hamiltonian as

$$\widehat{H} = \widehat{H}_1(\boldsymbol{r}_1) + \widehat{H}_2(\boldsymbol{r}_2) + \widehat{\mathcal{H}}(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{R}), \tag{16.113}$$

where the term $\widehat{\mathcal{H}}$ is due to the Coulomb interaction between the charge distributions of the two atoms. If we describe these charge distributions by means of their multipole moments, the interaction between the neutral atoms is given in a first approximation by the coupling of their instantaneous electric dipoles,

$$\widehat{\mathcal{H}} = \frac{e^2}{R^3}\left[\boldsymbol{r}_1 \cdot \boldsymbol{r}_2 - \frac{3(\boldsymbol{r}_1 \cdot \boldsymbol{R})(\boldsymbol{r}_2 \cdot \boldsymbol{R})}{R^2}\right]. \tag{16.114}$$

The next expansion terms, corresponding to dipole–quadrupole coupling (proportional to R^{-4}), quadrupole–quadrupole coupling (proportional to R^{-5}), and so on, are negligible at large distances compared to the dipole–dipole contribution.

To simplify the calculation, it is useful to take the z-axis in the direction of $\boldsymbol{R}$; $\widehat{\mathcal{H}}$ is then written as

$$\widehat{\mathcal{H}} = \frac{e^2}{R^3}\left[x_1 x_2 + y_1 y_2 - 2z_1 z_2\right]. \tag{16.115}$$

Assume that the atoms are in their ground state; if $\widehat{\mathcal{H}}$ is taken as a perturbation, the unperturbed wave function is $\psi_0 = \psi_0(\mathbf{r}_1)\psi_0(\mathbf{r}_2)$. Since the expectation value of the electric dipole moment of each atom in its ground state is zero, perturbation theory gives a zero correction to the first order, so the calculation must be carried over to the second order; this can be done, though not without some difficulty. Here we solve the problem using the variational method proposed by H. R. Hassé in 1930. We write the wave function in the form

$$\psi = \psi_0(\mathbf{r}_1, \mathbf{r}_2)(1 + v), \tag{16.116}$$

where the unknown function $v = v(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{R})$ is determined by requiring that $\langle \widehat{H} \rangle$ be a minimum. Since this wave function is not normalized, we use the expression $E \leq \langle \psi | \widehat{H} | \psi \rangle / \langle \psi | \psi \rangle$ to get (for v real),

$$\left(1 + 2\langle v \rangle + \langle v^2 \rangle\right) E \leq E_0 + 2E_0\langle v \rangle + 2\langle v\mathcal{H} \rangle + \langle v\widehat{H}v \rangle, \tag{16.117}$$

where all the expectation values are calculated using the unperturbed function ψ_0; in particular, E_0 is the sum of the energies of the two independent atoms. This expression shows that the problem is simplified by taking

$$v = \lambda\mathcal{H} \tag{16.118}$$

where λ is the variational parameter; substituting, we get

For intermediate distances, the situation is confusing and, for the moment, each case must be examined specifically.

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$$E \leq \frac{E_0 + 2\lambda\langle\mathcal{H}^2\rangle + \lambda^2\langle\mathcal{H}\widehat{H}_0\mathcal{H}\rangle}{1+\lambda^2\langle\mathcal{H}^2\rangle}. \tag{16.119}$$

A direct calculation shows that $\langle\mathcal{H}\widehat{H}_0\mathcal{H}\rangle$ vanishes, so we can write

$$E \leq \frac{E_0 + 2\lambda\langle\mathcal{H}^2\rangle}{1+\lambda^2\langle\mathcal{H}^2\rangle} = E_0 + \frac{\lambda(2-\lambda E_0)\langle\mathcal{H}^2\rangle}{1+\lambda^2\langle\mathcal{H}^2\rangle}. \tag{16.120}$$

The energy correction given by this expression has a minimum if $E_0 < 0$, which is the case for the real root of

$$(1+\lambda^2\langle\mathcal{H}^2\rangle)(1-\lambda E_0) = \lambda^2\langle\mathcal{H}^2\rangle(2-\lambda E_0). \tag{16.121}$$

Due to the smallness of the van der Waals forces, it is expected that $\langle\mathcal{H}^2\rangle \ll E_0^2$. Furthermore, it follows from Eq. (16.118) that for the perturbation to be small, it must be true that $|\lambda\mathcal{H}| \ll 1$, and therefore that $\lambda^2\langle\mathcal{H}^2\rangle \ll 1$. Taking this into account, the previous equation can be written to a sufficient approximation as $(1-\lambda E_0) = 0$, that is,

$$\lambda = \frac{1}{E_0}. \tag{16.122}$$

This value of λ gives

$$E \leq E_0 + \frac{\langle\mathcal{H}^2\rangle}{E_0}, \tag{16.123}$$

and an approximation to the ground-state wave function close to the optimum is

$$\psi = \psi_0(\mathbf{r}_1)\psi_0(\mathbf{r}_2)\left(1+\frac{\mathcal{H}}{E_0}\right). \tag{16.124}$$

The expectation value of $\mathcal{H}^2$ is easily determined by noting that in the ground state, $\langle x\rangle = 0$ and $\langle x^2\rangle = \frac{1}{3}\langle r^2\rangle = a_0^2$,

$$\langle\mathcal{H}^2\rangle = \frac{e^4}{R^6}\langle x_1^2x_2^2 + y_1^2y_2^2 + 4z_1^2z_2^2\rangle = \frac{6e^4a_0^4}{R^6}. \tag{16.125}$$

Since the ground-state energy of two H atoms is $E_0 = -e^2/a_0$, we finally have

$$E \leq E_0 - \frac{6e^2a_0^5}{R^6} = E_0\left(1+6\left(\frac{a_0}{R}\right)^6\right). \tag{16.126}$$

A more careful variational calculation shows that the correct value of the energy shift is obtained by writing 6.47 instead of the coefficient 6.

16.6.1.2 Retarded dispersion forces

At long distances, the R^{-6} dependence just obtained does not fully explain the observed behavior; this failure is usually attributed to the neglect of retardation effects. In 1948, Casimir and Polder showed that in the case of retardation effects due to the finite speed of propagation of electromagnetic interactions, Eq. (16.126) must be multiplied by a function of R which is unity at short distances, but becomes asymptotically C/R, so that the potential energy of the interaction varies as R^{-7} instead of R^{-6} at long distances. Such forces are called *retarded van der Waals–London forces* or *retarded dispersion* forces.

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16.6.2 Van der Waals and Casimir forces explained by SED

The Debye interactions can be understood in terms of the concepts of classical electrostatics. On the other hand, the van der Waals interaction, the Casimir forces and related effects are generally considered to owe their existence to the quantum fluctuations and thus to be quantum in origin. However, a more physically transparent picture can be obtained by considering these forces as a direct consequence of the existence of the real fluctuating vacuum, that is, the ZPF.

A simple way of expressing the idea behind the calculations is as follows. The ZPF in free space is an isotropic and homogeneous field with an average energy $\frac{1}{2}\hbar\omega$ per normal mode. But the presence of microscopic or macroscopic bodies – be they molecules, conducting plates, or the walls of a cavity – affects the field, as required by the laws of electrodynamics. Thus, the modes in a given region of space depend on the geometry and electric and magnetic properties of the bodies present, resulting in effective interactions between them, mediated by the ZPF. One such example was discussed in Section 10.2.1, namely the Casimir force between two neutral plates. In the following we briefly discuss the *retarded* Casimir effect from the same perspective.

16.6.2.1 Calculation of the Casimir–Polder force

As an illustration, we refer here to Boyer's (1969) calculation of the Casimir–Polder effect between two neutral polarizable bodies. The bodies attract each other because the dipole induced by the fluctuating field in one induces a dipole moment in the other, which in turn induces a dipole moment in the first. The R^{-6} energy term results from the interaction of these dipoles.

Let us focus on one of the modes of the field with frequency ω and energy $\frac{1}{2}\hbar\omega$: the presence of the two polarizable bodies produces a position-dependent change in the natural frequency and a concomitant change in the total energy of the ZPF, leading to an effective potential $U(R)$ between the particles. In short, the Casimir–Polder effect is the result of the modification of the dielectric constant K_0 of the vacuum to a higher value K, so the energy of the modes varies from $E_0 \sim K_0^2$ to $E \sim K^2$. Since in its turn the energy of a field mode is proportional to its frequency $E \sim \omega$, the frequency of each mode varies from ω_0 to $\omega = (K_0/K)^2\,\omega_0$.

To calculate $U(R)$, consider a conducting cavity containing particle A into which particle B is introduced. The second particle shifts the frequencies of the normal modes of oscillation, changing the total energy $\sum \frac{1}{2}\hbar\omega$ to $\sum \frac{1}{2}(\hbar\omega + \delta\omega)$. The shifts $\delta\omega$ are calculated taking into account the retardation. After a lengthy but transparent calculation, the result for the potential function is

$$U(R) = [-23(\alpha_A\alpha_B + \beta_A\beta_B) + 7((\alpha_A\beta_B + \beta_A\alpha_B))]\hbar c/4\pi R^7,$$

where α and β are the electric and magnetic polarizabilities, respectively. The R^{-7} potential arises thus as a result of the retarded effect of the second induced dipole on the first. This formula is identical to the one obtained by Feinberg and Sucher (1968) using quantum dispersion-theory techniques, but the SED calculation is considerably simpler and physically clear.

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16.7 Nuclear Structure. Extending the Periodic Table of the Elements

The systematic study of the properties of atomic nuclei shows that they have periodicities reminiscent of those of atoms. For example, the binding energy per nucleon has very pronounced maxima when the number of neutrons or protons is 2, 8, 20, 28, 50, 82, and so on. Nuclei with a number of protons or neutrons equal to one of the preceding "magic numbers" are particularly stable and consequently their relative abundance is large. Using the notation ${}_Z X^A$, where A is the mass number (number of protons plus neutrons), some magic nuclei are ${}_2\mathrm{He}$, ${}_8\mathrm{O}^{16}$, ${}_{20}\mathrm{Ca}^{40}$, ${}_{82}\mathrm{Pb}$. An example of particular stability is Pb, because while its isotope Pb^{204} accounts for only 1.4% of all existing lead, the "doubly magic" isotope Pb^{208} accounts for more than 52% (doubly magic means that the nucleus contains a magic number of protons and of neutrons at the same time).

The set of periodically recurring properties that distinguish magic (and doubly magic) nuclei suggests the possibility of describing the nucleus with a shell model similar to that of the atom; this is the basis of the theory developed by Göppert-Mayer and Jensen around 1950.[21] In a nuclear version of the Hartree–Fock method, each nucleon is considered to move in the common central potential produced by the rest of the nucleons; if this is the case, the choice of a reasonable short-range potential to model the effective potential of the self-consistent field should allow us to derive the magic numbers, taking into account the exclusion principle. This would be the nuclear transcription of the process that led to the atomic "magic numbers" 2 (He), 10 (Ne), 18(Ar),... using the Coulomb interaction, the independent-particle approximation and the Pauli principle.

As a first approximation we model the nuclear potential as a 3D rectangular well. This is adequate to describe the basic properties of the deuteron, ${}_1\mathrm{H}^2$, precisely because it is a short-range potential, which is one of the essential properties of the nuclear potential. The energy spectrum of particles bound by an infinite spherical potential well is shown in Table 16.4, where N_s represents the number of particles in the subshell $N_s = 2(2l + 1)$, and N the total (cumulative) number of particles. With the layer divisions suggested in Table 16.4, this model predicts the magic numbers 2, 8, 20, 40, 58,... the first three of which do indeed coincide with the empirical magic numbers, but for the rest the two sequences differ considerably. An analogous calculation using an isotropic harmonic oscillator potential yields the magic number sequence 2, 8, 20, 40, 70, 112,..., which is no better than the preceding one. The conclusion is that a short-range central potential cannot correctly predict all nuclear magic numbers, although it qualitatively agrees with the experimental situation. To improve the model it is necessary to introduce a noncentral potential, in particular the spin–orbit interaction.

[21] Maria Göppert-Mayer (1906–1972) was an outstanding German–US nuclear physicist. She developed a mathematical model for the structure of nuclear shells, which explained why certain numbers of nucleons result in particularly stable configurations. She was the second woman, after Marie Curie, to receive the Nobel Prize in Physics, which she shared in 1963 with Wigner and J. Hans D. Jensen (1907–1973) for their development of the nuclear shell model.

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Table 16.4 Parameters associated with the subshells for a particle bound by an infinite spherical potential well. The energy is expressed in units of $h^2/8\pi^2 ma^2$.

Subshell	E	N_s	N	Magic number
$1s$	9.9	2	2	
				2
$1p$	20.1	6	8	
				8
$1d$	33.2	10	18	
$2s$	39.5	2	20	
				20
$2p$	59.7	6	40	
				40
$1g$	67.0	18	58	
…	…	…	…	…

16.7.1 Introducing spin–orbit interaction

The results discussed earlier indicate that in order to correctly predict the magic numbers, one must partially break the degeneracy in l. The additional potential must depend on the orbital momentum, which suggests the introduction of a spin–orbit potential. The spin–orbit coupling can be considered to result from the interaction of the intrinsic (normal + anomalous) magnetic moment of the particle with the magnetic field produced by its own orbital motion. The formula

$$V_{SL} = -\frac{\hbar}{4m^2c^2}\left\langle \frac{1}{r}\frac{dV}{dr}\right\rangle \hat{\boldsymbol{\sigma}}\cdot\hat{\boldsymbol{L}}, \tag{16.127}$$

is derived directly from the Dirac equation; in Section 19.2 it is obtained for the specific case of the relativistic harmonic oscillator. The expectation values obtained from Eq. (16.127) are

$$\langle \hat{V}_{SL}\rangle = \begin{cases} V_0 l & \text{if } j = l + \frac{1}{2}, \\ -V_0(l+1) & \text{if } j = l - \frac{1}{2} \end{cases} \tag{16.128}$$

where

$$V_0 = -\frac{\hbar^2}{4m^2c^2}\left\langle \frac{1}{r}\frac{dV}{dr}\right\rangle. \tag{16.129}$$

The experimental data show that V_0 must be taken as positive, so that the levels with $j = l + 1/2$ fall below the levels with $j = l - 1/2$ (this is the opposite sign to that of atomic electrons). Fig. 16.11 shows the results obtained by assigning an appropriate value to this constant using the following phenomenological central potential, which lies between the square and the harmonic potentials,

$$V = \frac{V_1}{1 + e^{(r-R)/a}}. \tag{16.130}$$

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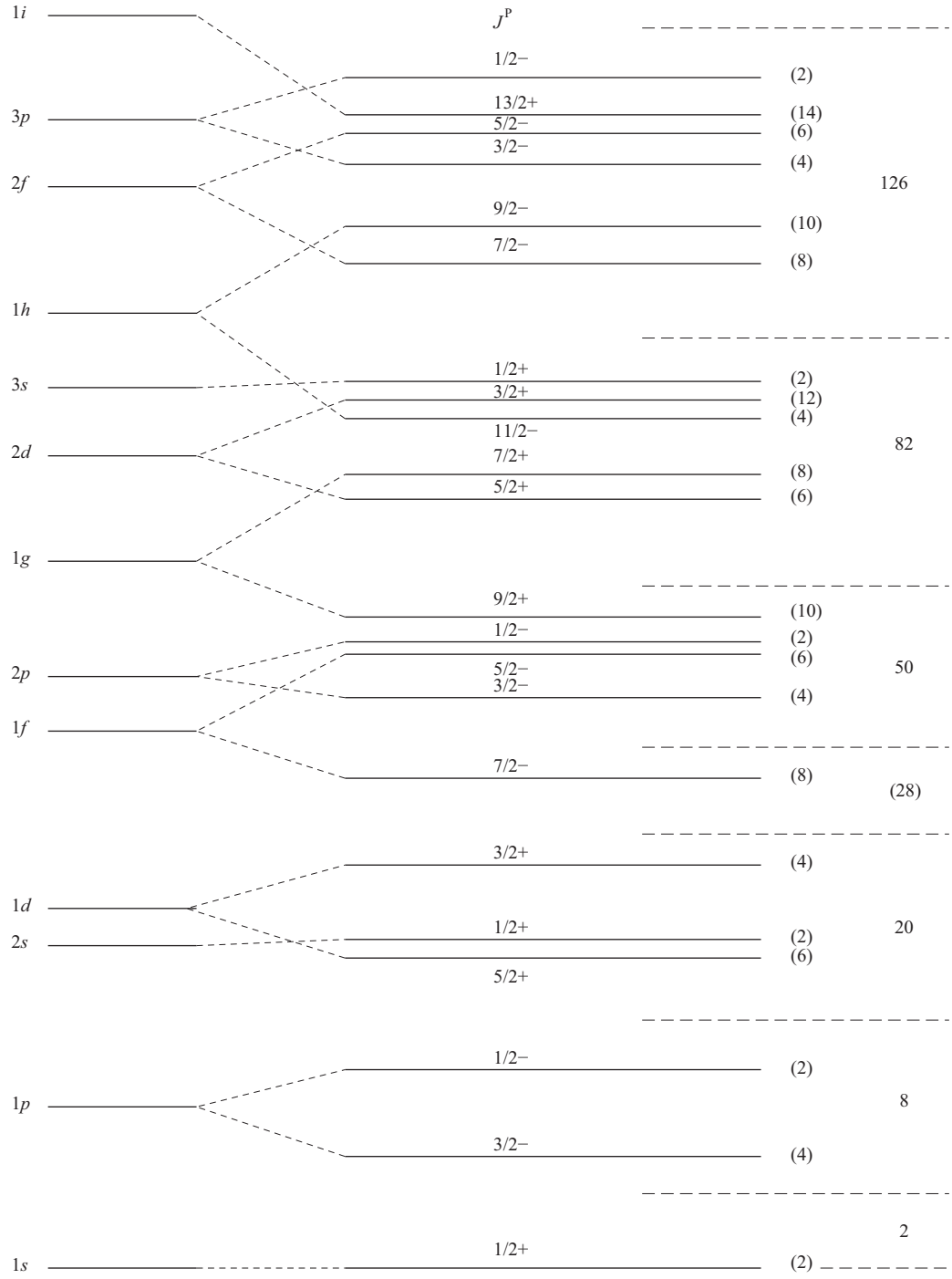


Figure 16.11 Energy levels of nucleons in an atomic nucleus according to the shell model. On the left are the values of (*nl*) and in the center those of J^P (P = parity). The dotted lines separate the layers. The penultimate column shows the number of neutrons or protons that fit into each subshell, and the column to the right shows the magic numbers predicted by this theory, which coincide with those found empirically (28 is sometimes considered "semimagic").

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In this expression the parameters V_1 and a are constant, while the radius of the nucleus R depends on the mass number A. From Fig. 16.11 we can see that the theory correctly predicts not only the magic numbers, but also the order in which the subshells with well-defined values of the total angular momentum J and of the parity P should appear: the first shell is filled with the nucleons in the state $1s_{1/2}$ ($J^P = 1/2$), the second shell is filled with equal particles in the states $1p_{3/2}$ and $1p_{1/2}$ ($J^P = 3/2$ and $1/2$, respectively), and so on.

The magic numbers of the nuclear shell model suggested the possibility of enhanced nuclear stability for some superheavy isotopes, particularly around atomic number 114 and neutron number 184, which would be doubly magic. This led to the hypothesis of the existence of an *island of stability* that could contain nuclides with half-lives of thousands, perhaps even millions of years. To this date (2025), the synthesis of nuclides too unstable to occur naturally on Earth has expanded the periodic table to 118 elements. While the lighter transuranic elements have found uses, the isotopes of those beyond ^{103}Lr (lawrencium), the so-called superheavy elements, are too unstable to exist outside the laboratory.

In its finished form, the shell model allows many properties of atomic nuclei to be correctly determined, despite its obvious approximate character and its phenomenological nature. Since the details of this subject are beyond the scope of the present text, we will not go into them here, but refer the interested reader to modern standard texts on nuclear physics.

Problems

P16.1 The neutral atoms F, Ca, and Rb have 9, 20, and 37 electrons, respectively. What is their electronic configuration in the ground state? What fundamental physical and chemical properties can be predicted for them?

P16.2 Prove directly that $\langle \text{ortho}|\boldsymbol{r}_1 + \boldsymbol{r}_2|\text{para}\rangle$ is zero for the He atom.

P16.3 In Section 16.3.3 we used the variational method to find the ground-state energy of helium using the trial function (16.43),

$$\psi = \frac{1}{\pi a_0^3} \exp\left(-\frac{r_1 + r_2}{a_0}\right), \tag{16.131}$$

where a_0 is the variational parameter. Try to modify this test function so that the error in the ground state energy does not exceed 0.5% of the experimental value. -78.97 eV.

P16.4 Use the wave function (16.131) to determine the electrostatic field generated by the helium atom in the space around it.

P16.5 Consider an isotropic 3D harmonic oscillator. Prove that in the N shell (N is the principal quantum number) there are $(N + 1)(N + 2)$ equal particles with spin 1/2. Use this information to show that the nuclear magic numbers predicted by the harmonic oscillator model are 2, 8, 20, 40, 70, and 112.

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P16.6 At large distances the binding potential of the H_2 molecule decreases exponentially, while the van der Waals force decreases as R^{-7}. What is the reason for this apparent discrepancy?

P16.7 Find the coefficients of the expansion of the electronic energy $\mathcal{E}(R)$ when it is modeled with the Morse potential

$$\mathcal{E}(R) = D[e^{-2(R-R_0)/a} - 2e^{-(R-R_0)/a}], \tag{16.132}$$

up to and including the fourth order.

P16.8 Find the order of magnitude of the wavelength of the radiation emitted during a $K = 1 \rightarrow K = 0$ vibrational transition in a LiH molecule. Assume that the equilibrium distance between the atoms in a diatomic molecule is similar to the distance between the atoms in a crystal of the same substance. *Note*: The LiH lattice is cubic and the crystal has an approximate density of 0.83 g/cm^{-3}.

(Solution: $\lambda \sim 1.8 \times 10^{-3}$cm)

P16.9 Based on the absorption spectrum of HCl vapor in the near infrared shown in Figure 16.8(b), prove that the equilibrium distance between the H and Cl atoms of this molecule is of the order of 1.3×10^{-8} cm.

P16.10 Find the dissociation energy of the D_2 molecule, using the fact that the dissociation energy and the minimum vibrational energy of the H_2 molecule are equal to 4.46 eV and 0.26 eV, respectively.

P16.11 Prove that the molecule He_2^{3+} does not exist.

P16.12 An empirical formula for the potential of the NaCl molecule is

$$V = -\frac{e^2}{4\pi\varepsilon_0 R} + Ae^{-R/a}, \tag{16.133}$$

where R is the internuclear distance. The equilibrium internuclear distance is 2.5 Å and the dissociation energy is 3.6 eV. Find the value of A and a/R_0, and explain the physical meaning of the parameters A and a.

P16.13 Compare the rotational and vibrational levels of an HCl molecule calculated with the potential

$$V(r) = 4\alpha\left[\left(\frac{d}{r}\right)^{12} - \left(\frac{d}{r}\right)^{6}\right], \quad \alpha = 3.1\times10^{-12}\,\text{eV}, \quad d = 3.3\,\text{Å}. \tag{16.134}$$

Hint: Since the equilibrium position r_0 depends weakly on angular momentum, the effective potential can be expanded around r_0. It is convenient to introduce $b = \hbar^2/md^2$ and express the potential in terms of b and $x_0 = r_0/d$.

P16.14 The vibrational frequency of the CO molecule in its lowest state is $\nu_0 = 2 \times 10^{13}$ Hz. What is the wavelength of the radiation emitted by the lowest vibrational excitation? What is the probability that the first vibrational state is excited? Compare your result with the probability that the CO molecule is in its vibrational ground state when the temperature is 300 K.

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Bibliographical Notes

For a general treatment of the chemical bond, we recommend the classic book by Linus Pauling (1960).

For the latest release of the periodic table (dated 4 May 2022), see https://iupac.org/what-we-do/periodic-table-of-elements/#a10.

For an interactive periodic table of the isotopes, see https://ciaaw.org/periodic-table-isotopes.html

For a more detailed discussion of intermolecular forces, we refer the reader to specialist texts in physical chemistry, such as Israelachvili (2011).

For a comprehensive account of Casimir effect experiments, see Lamoreux (2005).

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