

I.

Potential Energy Functions

Potential energy functions that control nuclear motions in various forms of matter provide a central object of theoretical attention in the formalism to be developed in subsequent chapters. The quantum mechanics of electrons interacting with the nuclei provides the source of those potential energy functions. It is natural, then, to begin this volume that is devoted to multi-dimensional potential energy landscapes and their implications by reviewing the relevant underlying quantum mechanical fundamentals. Understanding these fundamentals is a necessary prerequisite for selecting many-body models that are typically used for analytical theory, for computer simulation, and for interpreting experimental observations of a wide range of material systems, both in and out of thermal equilibrium. This chapter includes a survey of some of the commonly encountered model potentials and discusses their principal characteristics for representing both “simple” and “complex” substances.

A complete review of quantum mechanical basics would include relativistic effects that become important when heavy elements with high nuclear charges are present. However, the development to follow is limited to the nonrelativistic regime that is described by the Schrödinger equation. For present purposes, this is a justifiable simplification because it is quantitatively accurate for many applications, and even when relativistic effects exist, this nonrelativistic approximation can still qualitatively capture the majority of properties needed for the development of the energy landscape/inherent structure formalism.

A. Quantum Mechanical Basis

The natural starting point for consideration of condensed-matter properties is the quantum mechanics of the constituent electrons and nuclei, regarded as point particles with fixed masses and electrostatic charges. The dynamical evolution of collections of these point particles is described by the time-dependent Schrödinger equation [Pauling and Wilson, 1935; Schiff, 1968]:

$$\mathbf{H}\Psi = -(\hbar/i)(\partial\Psi/\partial t) \quad (\text{I.1})$$

This basic partial differential equation is to be solved subject to applicable initial and boundary conditions, where the system volume in general may be either finite or infinite. Here the Hermitian operator \mathbf{H} is the spin-independent Hamiltonian operator for the collection of electrons and nuclei, Ψ is the time-dependent wave function for that collection, and \hbar is Planck's constant h divided by 2π . In addition to time t , Ψ also has as its variables the set of electronic and nuclear

coordinates, to be denoted respectively by $\{\mathbf{x}'_i\} \equiv \{\mathbf{r}'_i, s'_i\}$ and $\{\mathbf{x}_j\} \equiv \{\mathbf{r}_j, s_j\}$, where these coordinates include both spatial positions (\mathbf{r}' , \mathbf{r}), and spins if any (s' , s). Because of the linearity of the Schrödinger equation, Ψ can be resolved into a linear combination of components corresponding to each of the eigenfunctions of the time-independent wave equation.

$$\Psi(\{\mathbf{x}'_i\}, \{\mathbf{x}_j\}, t) = \sum_n A_n \psi_n(\{\mathbf{x}'_i\}, \{\mathbf{x}_j\}) \exp(-iE_n t/\hbar) \quad (1.2)$$

$$[\mathbf{H} - E_n] \psi_n(\{\mathbf{x}'_i\}, \{\mathbf{x}_j\}) = 0$$

In these expressions, n indexes the time-independent spin and space eigenfunctions ψ_n with respective energy eigenvalues E_n . The constants A_n are determined by the initial state of the system under consideration. Because \mathbf{H} is spin independent, each ψ_n can also be chosen simultaneously as an eigenfunction of total spin-squared (\mathbf{S}^2) and directionally projected spin operators (\mathbf{S}_z) for the electrons and each nuclear species present. The ψ_n are obliged to exhibit the exchange symmetries required for the particle types that are present (symmetric for identical bosons, antisymmetric for identical fermions).

A basic simplification upon which the formalism to be developed in this volume rests is the separation of electronic and nuclear degrees of freedom in the full wave mechanics, using the Born-Oppenheimer approximation [Born and Oppenheimer, 1927]. This approximation is motivated and justified by the wide discrepancy between the mass m_e of the light electrons on one side and the masses M_j of the much heavier nuclei on the other. In the hypothetical limit for which all ratios m_e/M_j of electron to nuclear masses approach zero, the eigenfunction and eigenvalue errors committed by the Born-Oppenheimer approximation would also asymptotically approach zero [Takahashi and Takatsuka, 2006]. In most applications to be considered in this text, the actual errors attributable to the Born-Oppenheimer approximation with nonzero mass ratios are in fact negligibly small.

To apply the Born-Oppenheimer approximation, the full Hamiltonian operator \mathbf{H} is first separated into two parts,

$$\mathbf{H} = \mathbf{H}_I + \mathbf{H}_{II}, \quad (1.3)$$

where \mathbf{H}_I refers to motion of electrons in the presence of fixed nuclei, and \mathbf{H}_{II} collects all remaining terms (nuclear kinetic energy, and nuclear pair Coulomb interactions). Because the full Schrödinger Hamiltonian \mathbf{H} is spin-independent, and if no external forces are present, the specific forms are

$$\mathbf{H}_I = -(\hbar^2/2m_e) \sum_i \nabla_{\mathbf{r}'_i}^2 - e^2 \sum_i \sum_k Z_k / |\mathbf{r}'_i - \mathbf{r}_k| + e^2 \sum_{i < j} 1/r'_{ij}, \quad (1.4)$$

and

$$\mathbf{H}_{II} = -\hbar^2 \sum_j (\nabla_{\mathbf{r}_j}^2 / 2M_j) + e^2 \sum_{j < k} Z_j Z_k / r_{jk}. \quad (1.5)$$

As indicated earlier, the \mathbf{r}'_i in these equations denotes spatial positions of the electrons, and the \mathbf{r}_j does the same for spatial positions of the nuclei. Following normal convention, e represents the fundamental Coulomb charge of a proton, and the nuclei bear respective charges $Z_j e$. This separation permits the full quantum mechanical problem to be resolved into an ordered sequence of two simpler problems. In the first stage, eigenfunctions and eigenvalues are obtained just for the

operator \mathbf{H}_I , i.e., for the electrons moving in the static Coulomb field supplied by the nuclei at fixed positions, with those electronic eigenfunctions subject to the necessary antisymmetry conditions [Pauling and Wilson, 1935; Schiff, 1968]:

$$[\mathbf{H}_I - E_{n'}^{(el)}(\{\mathbf{x}_j\})]\psi_{n'}^{(el)}(\{\mathbf{x}'_i\} | \{\mathbf{x}_j\}) = 0. \quad (\text{I.6})$$

As the vertical-bar notation for the wavefunctions emphasizes, the entire set of electronic eigenfunctions and eigenvalues depends parametrically on the nuclear coordinates. For each electron-subsystem indexing quantum number n' there exists a well-defined limit for the eigenvalue as all nuclei recede from one another to infinity:

$$E_{n'}^{(el)}(\infty) = \lim_{\{r_{kl}\} \rightarrow \infty} E_{n'}^{(el)}(\{\mathbf{x}_j\}). \quad (\text{I.7})$$

This limiting energy consists of a sum of independent contributions from the individual atoms and/or ions that are formed as the electrons become partitioned and localized around the widely separated nuclei.

The second stage of the solution sequence addresses the nuclear quantum mechanics. This involves the operator \mathbf{H}_{II} augmented by the relevant position-dependent energy eigenvalue from the electron subsystem. Consequently, the effective nuclear Hamiltonian becomes

$$\mathbf{H}^{(nuc)} = -\hbar^2 \sum_j (\nabla_{\mathbf{r}_j}^2 / 2M_j) + \Phi(\{\mathbf{r}_j\} | n'). \quad (\text{I.8})$$

Here $\Phi(\{\mathbf{r}_j\} | n')$ is the Born-Oppenheimer potential energy (hyper)surface on which the nuclei move:

$$\Phi(\{\mathbf{r}_j\} | n') = e^2 \sum_{j < k} Z_j Z_k / r_{jk} + E_{n'}^{(el)}(\{\mathbf{x}_j\}) - E_{n'}^{(el)}(\infty). \quad (\text{I.9})$$

Notice that $E_{n'}^{(el)}(\infty)$ has been inserted into Φ to provide a convenient energy origin for the nuclear subsystem. In other words, this convention implies that $\Phi = 0$ when all nuclei are infinitely far from one another. Nuclear eigenfunctions and eigenvalues (indexed by n'') are subsequently to be determined by solving the nuclear Schrödinger equation:

$$[\mathbf{H}^{(nuc)} - E_{n''}^{(nuc)}(n')]\psi_{n''}^{(nuc)}(\{\mathbf{x}_j\} | n') = 0, \quad (\text{I.10})$$

subject to given boundary conditions, and to symmetry requirements imposed by the presence of identical nuclei with identical spin components (symmetric under exchange for bosons, antisymmetric under exchange for fermions) [Pauling and Wilson, 1935, Chapter XIV; Landau and Lifshitz, 1958a, Chapter IX].

As a consequence of this sequential solution process, the Born-Oppenheimer approximations to the full-system eigenfunctions and eigenvalues have the following forms:

$$\psi_n(\{\mathbf{x}'_i\}, \{\mathbf{x}_j\}) \cong \psi_{n'}^{(el)}(\{\mathbf{x}'_i\} | \{\mathbf{x}_j\}) \psi_{n''}^{(nuc)}(\{\mathbf{x}_j\} | n'); \quad (\text{I.11})$$

$$E_n \cong E_{n'}^{(el)}(\infty) + E_{n''}^{(nuc)}(n'). \quad (\text{I.12})$$

The index (“quantum number”) n for the initial problem has been replaced by the pair n' , n'' for electronic and nuclear problems, respectively. It is possible and usually convenient to take the electronic wave functions to be real and orthonormal among themselves for any nuclear configuration.

Because of the presence of unbound electrons in highly excited states, this method requires that the system be at least temporarily confined to a finite volume V , which can be allowed to pass to infinity at a later stage. Consequently one can write

$$\int \psi_{m'}^{(el)}(\{\mathbf{x}'_i\} | \{\mathbf{x}_j\}) \psi_{n'}^{(el)}(\{\mathbf{x}'_i\} | \{\mathbf{x}_j\}) d\{\mathbf{x}'_i\} = \delta(m', n'). \quad (\text{I.13})$$

The same can be assumed true for the nuclear eigenfunctions for any given electronic quantum state n' :

$$\int \psi_{m''}^{(nuc)}(\{\mathbf{x}_j\} | n') \psi_{n''}^{(nuc)}(\{\mathbf{x}_j\} | n') d\{\mathbf{x}_j\} = \delta(m'', n''). \quad (\text{I.14})$$

The “integrations” indicated in these last two equations implicitly include spin summations where necessary. The notation $\delta(j, k)$ stands for the Kronecker delta function (equal to unity for $j = k$, zero otherwise).

In parallel with Eq. (I.2), the time dependence of the nuclear quantum dynamics on the n' electronic potential surface can then be expressed as follows:

$$\Psi^{(nuc)}(\{\mathbf{x}_j\}, t | n') = \sum_{n''} B_{n''} \psi_{n''}^{(nuc)}(\{\mathbf{x}_j\} | n') \exp[-iE_{n''}(n')t/\hbar], \quad (\text{I.15})$$

with numerical coefficients $B_{n''}$ determined by initial conditions. In circumstances where very heavy nuclei are involved, moving through regions of the configuration space where potential Φ varies slowly with position, quantum dynamics often can be replaced by its classical limit. The corresponding Newtonian equations of motion for the N nuclei then describe the nuclear configurational dynamics [Goldstein, 1953]:

$$M_j d^2 \mathbf{r}_j(t) / dt^2 = -\nabla_{\mathbf{r}_j} \Phi(\mathbf{r}_1 \dots \mathbf{r}_N | n') \quad (1 \leq j \leq N). \quad (\text{I.16})$$

One might legitimately question whether the “bare” nuclear masses M_j that appear in Eqs. (I.8) and (I.16) are appropriate or whether a set of effective masses M_j^* that include contributions from the electron subsystem would lead to a more precise description. If the electrons are in their lowest energy (ground) state, or in a low-lying excited state, each nucleus would tend to have bound to it a number of electrons equal, or nearly equal, to its atomic number Z_j . Because these bound electrons would preferentially move with that nucleus, their mass should in principle be added to the bare nuclear mass. Thus, if the physical system of interest corresponds to well-separated electrostatically neutral atoms (e.g., noble gas atoms), the effective masses would be

$$M_j^* = M_j + Z_j m_e, \quad (\text{I.17})$$

where m_e is the electron mass. If the nuclei exist within the system as ions with fixed oxidation states (electrostatic charges), then expression (I.17) would have to be modified accordingly to account for the deficit or surfeit of electrons compared to the atomic number Z_j . Chemical bonding to produce molecular species or extended covalent networks within which included nuclei execute vibrational motions present a more complicated situation; detailed calculations would be necessary to reveal the extent to which electron mass follows the vibrating nuclei, and thus to assign appropriate effective masses. In any case, these effective mass corrections to the Born-Oppenheimer approximation are small in absolute magnitude but should be carefully considered when high-accuracy theory and/or calculations are contemplated.

Each of the Born-Oppenheimer potential functions $\Phi(\mathbf{r}_1 \dots \mathbf{r}_N | n')$ can be viewed as defining a hypersurface embedded in a $(3N + 1)$ -dimensional space that is generated by the $3N$ Cartesian coordinates of nuclear position supplemented by an energy axis. Because many of the basic interests of condensed matter science require N to be roughly comparable to Avogadro's number ($\approx 6.022 \times 10^{23}$), these hypersurfaces are enormously complicated. Nevertheless, mathematical description at least of a statistical sort is feasible for these hypersurfaces, and it is facilitated to some extent by analogies to the topographies of familiar three-dimensional landscapes. A substantial portion of the analyses presented in subsequent chapters exploits this viewpoint.

Although it proves to be an excellent description for many problems in condensed-matter physics and chemical physics, the Born-Oppenheimer approximation is inaccurate and thus inappropriate in some special circumstances. In addition to the effective-mass corrections mentioned above, one of these cases involves nuclear dynamics where close approach (in energy), or even intersection, of two or more potential energy hypersurfaces occurs [Yarkony, 1996, 2001; Domcke and Yarkony, 2012]. Another important case concerns superconductivity arising from the BCS mechanism of electron coupling through phonons [Bardeen, Cooper, and Schrieffer, 1957], and in fact the relevant deviations from the Born-Oppenheimer description underlie the nuclear isotopic-mass dependence of superconducting transition temperatures [Kittel, 1963, Chapter 8; Ashcroft and Mermin, 1976, Chapter 34].

B. Properties of Electronic Ground and Excited States

Although the number of electronic eigenstates indexed by n' in the Born-Oppenheimer approximation is infinite for all material systems of interest and includes states of unbounded excitation energy above the ground state, the principal focus of attention in the present volume is on the ground state itself, and the low-lying excited states. If the atoms comprised in a many-body system are geometrically well isolated from one another, the lowest lying electronic states are nearly degenerate (i.e., confined to very narrow bands) and have energies substantially determined by those of the separate atoms. Bound excited states for isolated atoms are limited above by that atom's ionization energy. Table I.1 presents the ionization energies for individual atoms of several elements, i.e., the energy difference between the electronic ground state and the lowest lying ionized continuum state for those atoms. The substantial variation among entries for the elements is an indication of their distinctive chemical properties.

As a configuration of many identical atoms, initially widely separated from one another, is uniformly compressed, the narrow bands of nearly degenerate energy levels of the many-atom system tend to broaden in a manner strongly dependent on the specific atomic elements involved. When brought to normal ambient-pressure crystal densities and configurations, different elements

TABLE I.1. Ionization energies (in eV) for individual atoms of several elements^a

Element	H	He	Li	C	O	Na	Si
Ionization energy	13.59844	24.58741	5.39172	11.26030	13.61806	5.13908	8.15169

^aLide, 2003, p. 10–178.

can become electronic insulators (large remaining band gap between ground and lowest lying excited electronic state), semiconductors (small but nonzero band gap), or metals (no gap) [Harrison, 1980]. But it is well to keep in mind that even atomic species that are normally regarded as insulators (e.g., the noble gases) eventually become metallic materials under sufficiently strong compression. A case in point is the element xenon, which has been reported to transform to a metallic ground state at a pressure of 132(5) GPa [Goettal et al., 1989].

Electronic excitation affects the occurrence and nature of potential energy minima. This is a phenomenon present even in the simplest molecular systems and is illustrated by the elementary example of molecular hydrogen. Figure I.1 shows a plot of the single-molecule potential energy curves for H_2 , as a function of internuclear separation, for the $^1\Sigma_g^+$ ground state (electron spin singlet) and the lowest lying $^3\Sigma_u^+$ (electron spin triplet) excited state. This pair of curves vividly demonstrates the disappearance of a well-developed covalent chemical bond minimum upon excitation from the ground state, with replacement by a repulsive potential curve. For strict accuracy, it should be mentioned that even the repulsive $^3\Sigma_u^+$ curve possesses an extremely shallow minimum at very large internuclear separation because of very weak dispersion attraction between well-separated hydrogen atoms [Landau and Lifshitz, 1958a, p. 270; Kołos and Wolniewicz, 1965]. The two-electron example illustrated in Figure I.1 is the simplest case of a more general result for a spin-independent Schrödinger Hamiltonian, specifically that the lowest energy eigenvalue occurs when the net electron spin is at its lowest because of the Pauli exclusion principle

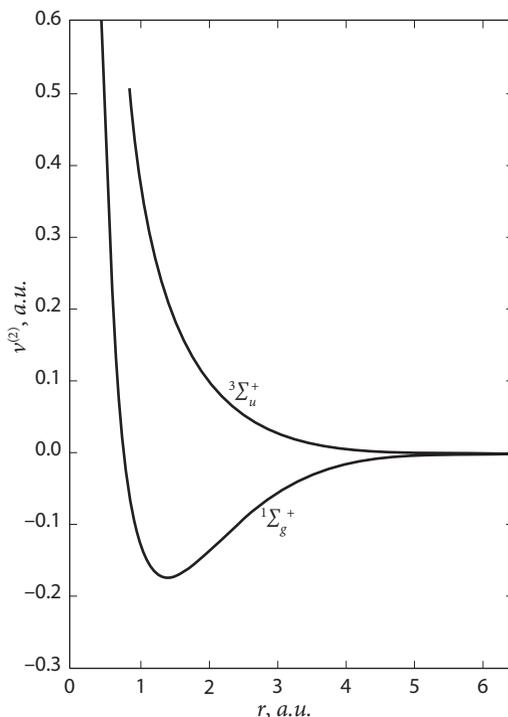


FIGURE I.1. Potential energy curves for the singlet ground state and the lowest lying triplet excited state of molecular hydrogen [Kołos and Wolniewicz, 1965]. The scales involve atomic units (“a.u.”), where for distance 1 a.u. equals the Bohr radius 0.5292 Å, and for energy 1 a.u. equals 27.21 eV.

(Pauli, 1925). In most applications to be considered later in this text, that is the electronic state involved.

The Hellmann-Feynman theorem, which is applicable to any electronic eigenstate, can be used to provide valuable insight into the nature of interparticle interactions [Hellmann, 1937; Feynman, 1939; Weissbluth, 1978]. This theorem concerns the change in an electronic eigenvalue as a result of a differential perturbation in the electronic Hamiltonian operator \mathbf{H}_I (Eq. (I.4)). Let λ represent the strength of that perturbation. The Hellmann-Feynman theorem states the following:

$$dE_{n'}^{(el)}(\{\mathbf{x}_j\})/d\lambda = \int \psi_{n'}^{(el)}(\{\mathbf{x}_i'\} | \{\mathbf{x}_j\}) [d\mathbf{H}_I/d\lambda] \psi_{n'}^{(el)}(\{\mathbf{x}_i'\} | \{\mathbf{x}_j\}) d\{\mathbf{x}_i'\}. \quad (\text{I.18})$$

That is, the rate of change with λ of the n' electronic eigenvalue is precisely equal to the diagonal matrix element in that eigenstate of the corresponding rate of change of the electronic Hamiltonian operator \mathbf{H}_I . The specific application of this result that is useful in the present context identifies the perturbation as a spatial shift in one of the nuclear positions, say \mathbf{r}_l for nucleus l . As a result, Eq. (I.18) implies the following result:

$$\nabla_{\mathbf{r}_l} E_{n'}^{(el)}(\{\mathbf{x}_j\}) = \int [\psi_{n'}^{(el)}(\{\mathbf{x}_i'\} | \{\mathbf{x}_j\})]^2 \left[-Z_l e^2 \nabla_{\mathbf{r}_l} \sum_i 1/|\mathbf{r}_i' - \mathbf{r}_l| \right] d\{\mathbf{x}_i'\} \equiv -\mathbf{F}_l^{(Coul)}(n'). \quad (\text{I.19})$$

This equation declares that the rate of change of the electronic eigenvalue $E_{n'}^{(el)}$, with respect to a shift in position of nucleus l , is precisely the negative of the coulombic force exerted on nucleus l by the charge distribution of the electrons in that quantum state n' . In this respect, the electronic contribution to Born-Oppenheimer potential energy surfaces has a simple interpretation in terms of classical electrostatics. As a special case, if all nuclei are at positions of mechanical equilibrium, the net electrostatic force on each of those nuclei caused by the electron density and the other nuclei must vanish identically. More generally, in the case of a nearby pair of atoms engaging in a covalent chemical bond, whether or not those atoms are at positions of mechanical equilibrium, Eq. (I.19) places a constraint on the distribution of electron density in the vicinity of that pair.

The quantum mechanical virial theorem [Born, Heisenberg, and Jordan, 1925–1926; Slater, 1933; Hirschfelder, Curtiss, and Bird, 1954] for a collection of electrons and nuclei establishes a rigorous connection between the overall kinetic energy operator

$$\mathbf{K} = -(\hbar^2/2m_e) \sum_i \nabla_{\mathbf{r}_i}^2 - \hbar^2 \sum_k (\nabla_{\mathbf{r}_k}^2/2M_k), \quad (\text{I.20})$$

and the virial operator

$$\mathbf{V} = \sum_i \mathbf{r}_i' \cdot \mathbf{F}_i' + \sum_k \mathbf{r}_k \cdot \mathbf{F}_k. \quad (\text{I.21})$$

Here, \mathbf{F}_i' and \mathbf{F}_k , respectively, are the vector forces experienced by electron i and by nucleus k for any given spatial configuration of all electrons and nuclei. Presuming that this system is confined to the interior of a container with reflecting walls, and is in overall quantum state n , the theorem declares

$$\int \psi_n^* \mathbf{K} \psi_n d\{\mathbf{x}_i'\} d\{\mathbf{x}_k\} = -(1/2) \int \psi_n^* \mathbf{V} \psi_n d\{\mathbf{x}'\} d\{\mathbf{x}_k\}. \quad (\text{I.22})$$

Note that this theorem does not rely upon the Born-Oppenheimer approximation but is a general statement about eigenstates for the combined quantum mechanics of electrons plus nuclei. If the quantum state denoted by n is a bound state inside an arbitrarily large container and has vanishing

center-of-mass motion, then the only forces present are those between pairs of electrons and/or nuclei. Because those forces arise exclusively from Coulomb interactions, the virial operator is equivalent to the sum of all of those Coulomb terms:

$$\begin{aligned} \mathbf{V} &\rightarrow e^2 \sum_{i < j} 1/r_{ij}' - e^2 \sum_i \sum_k Z_k / |\mathbf{r}_i' - \mathbf{r}_k| + e^2 \sum_{k < l} Z_k Z_l / r_{kl} \\ &\equiv \mathbf{V}_{Coul}. \end{aligned} \quad (I.23)$$

In this circumstance, Eq. (I.22) states that the expectation value of the total kinetic energy is minus one-half that of the total Coulomb interaction:

$$\int \psi_n^* \mathbf{K} \psi_n d\{\mathbf{x}_i'\} d\{\mathbf{x}_k\} = -(1/2) \int \psi_n^* \mathbf{V}_{Coul} \psi_n d\{\mathbf{x}_i'\} d\{\mathbf{x}_k\}. \quad (I.24)$$

In the formal limit where masses of all the nuclei approach infinity, those nuclei can remain localized at vanishing-force mechanical equilibrium points of the Born-Oppenheimer potential energy surface $\Phi(\{\mathbf{r}_k\}|n')$, and they would have no kinetic energy. As a result, the left side of Eq. (I.24) involves only electron kinetic energy, whereas the right side contains electron–electron, electron–nucleus, and nucleus–nucleus contributions. Alternatively, suppose that the nuclei were constrained at positions not necessarily those of mechanical equilibrium on the Born-Oppenheimer potential energy surface but just acted as fixed force centers for the electron quantum mechanics. This is the situation for the first stage of the Born-Oppenheimer approximation outlined in Section I.A of this chapter. With the resulting nonvanishing net forces on the nuclei, the virial theorem then states the following for the electronic degrees of freedom:

$$\sum_k \mathbf{r}_k \cdot \nabla_{\mathbf{r}_k} \Phi(\{\mathbf{r}_l\}|n') = \int \psi_n^{(el)*} \left\{ \sum_i [-(\hbar^2/m_e) \nabla_{\mathbf{r}_i}^2 + \mathbf{r}_i' \cdot \mathbf{F}_i'] \right\} \psi_n^{(el)} d\{\mathbf{x}_j'\}. \quad (I.25)$$

This equation indicates that the first spatial moment of the forces on the nuclei is proportional to the imbalance in kinetic and virial-force contributions of the electronic degrees of freedom.

A final application of the quantum virial theorem concerns the case of a macroscopic system confined to a small enough region V that it exerts nonvanishing forces on the constraining walls. These wall forces can be interpreted as a normal outward pressure p , and their presence requires that the virial operator \mathbf{V} be separated into a part internal to the system of electrons and nuclei (*Coul*), and a part involving the external-wall interactions (*ex*):

$$\mathbf{V} = \mathbf{V}_{Coul} + \mathbf{V}_{ex}. \quad (I.26)$$

As a result, the theorem leads to a formal expression for the pressure–volume product pV for the system in quantum state n :

$$3pV = \int \psi_n^* [2\mathbf{K} + \mathbf{V}_{Coul}] \psi_n d\{\mathbf{x}_i'\} d\{\mathbf{x}_k\}. \quad (I.27)$$

This is another result whose validity does not rely on the Born-Oppenheimer approximation.

C. Mathematical Attributes of Potential Energy Functions

Whether it is the electronic ground state or any of the electronic excited states that is under consideration, it is important to recognize the general mathematical properties that must be obeyed

by the corresponding Born-Oppenheimer potential energy functions that control nuclear motions. These general properties in turn influence the statistical behavior of the corresponding condensed-matter systems. Here is a list of the most basic of those general properties. Some are obvious, others more subtle, but all provide a necessary background for the theoretical developments of the next two sections, I.D and I.E, and of subsequent chapters.

- (1) For any quantum state, the potential energy function Φ is a single-valued function of the nuclear position coordinates $\mathbf{r}_1 \dots \mathbf{r}_N$.
- (2) Any geometrically isolated set of nuclei in free space (i.e., remote from container walls) can be translated and/or rotated arbitrarily without changing the value of the potential energy function Φ .
- (3) Permutation of the positions of any pair of nuclei with equal atomic numbers ($Z_j = Z_p$, but possibly different isotopes) leaves the potential energy function Φ unchanged. This invariance remains valid even in the presence of wall forces.
- (4) The electrostatic charges $Z_j e$ carried by the nuclei cause coulombic divergences in the $\Phi(\mathbf{r}_1 \dots \mathbf{r}_N | n')$ whenever the separation between two nuclei tends to zero. Specifically,

$$\Phi(r_{jk} \rightarrow 0 | n') \sim Z_j Z_k / r_{jk} + A(\mathbf{r}_1 \dots \mathbf{r}_N | n'), \quad (\text{I.28})$$

where the function A remains finite in that nuclear confluence limit. For virtually all condensed-matter applications of interest, the instances of r_{jk} remain large enough even at their smallest occurrences that these nuclear Coulomb singularities are obscured by powerful (but bounded) electron-cloud overlap repulsions. The latter are implicit in the A function.

- (5) Aside from rare nuclear configurations producing electronic degeneracies such as “conical intersections” [Yarkony, 1996, 2001; Domcke and Yarkony, 2012], Φ is continuous and at least twice differentiable in nuclear position coordinates $\mathbf{r}_1 \dots \mathbf{r}_N$ away from any nuclear coincidences. In particular, this phenomenon implies that relative or absolute minima of Φ are locally at least quadratic in those nuclear coordinates. Such minima are mechanically stable configurations, that is, forces on all nuclei vanish. These Φ minima are henceforth called “inherent structures” throughout the remainder of this text.
- (6) Φ obeys a global stability criterion [Fisher and Ruelle, 1966; Ruelle, 1969, p. 33]. There exists some $K > 0$ that is independent of N , of $\mathbf{r}_1 \dots \mathbf{r}_N$, of boundary conditions, and of quantum number n' such that

$$\Phi > -KN. \quad (\text{I.29})$$

This property stands in accordance with the common observation that cohesive energy of a macroscopic material sample at fixed number density is an extensive quantity, i.e., proportional to sample size.

- (7) If the system is constrained to overall charge neutrality, and if all pairs of nuclei are constrained to be more widely separated than some minimum distance $r_0 > 0$, then in the $N \rightarrow \infty$ asymptotic regime, Φ must possess the extensivity property, i.e., it can increase in magnitude no more rapidly than proportionally to N . This condition is consistent with, but independent of, the previous condition (6).

- (8) In a large system of N nuclei, configurational rearrangements involving only a small local subset of $O(1)$ nuclei change Φ only by $O(1)$. Removal to infinity of $O(1)$ nuclei is one example of this limited change in Φ .

A useful context in which to view model potentials includes the general resolution of a many-body potential function $\Phi(\mathbf{r}_1 \dots \mathbf{r}_N | n')$ into one-body, two-body, three-body, ..., N -body contributions:

$$\Phi(\mathbf{r}_1 \dots \mathbf{r}_N | n') \equiv \sum_{i=1}^N v^{(1)}(\mathbf{r}_i) + \sum_{i=2}^N \sum_{j=1}^{i-1} v^{(2)}(\mathbf{r}_i, \mathbf{r}_j) + \sum_{i=3}^N \sum_{j=2}^{i-1} \sum_{k=1}^{i-1} v^{(3)}(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) + \dots + v^{(N)}(\mathbf{r}_1 \dots \mathbf{r}_N). \quad (\text{I.30})$$

For notational simplicity, this expression assumes that all nuclei are the same species, but the multicomponent extension is straightforward. By requiring Eq. (I.30) to be an identity successively for $N = 1, 2, 3, \dots$ the $v^{(1)}, v^{(2)}, v^{(3)}, \dots$ in turn each receive precise definitions. Specifically each $v^{(l)}$ for a set of l nuclei corrects the estimate of the potential energy for that set provided by the collection of lower order $v^{(j)}$ functions. Because the coordinates \mathbf{r}_i refer to single nuclei, the single-particle contributions $v^{(1)}$ would describe interactions with external force fields, such as those associated with containment vessel walls or with a gravitational field. If the circumstances are appropriate, the series of terms in identity (I.30) may decline in magnitude sufficiently rapidly with superscript order that truncation may be a reasonable approximation at some fixed order $l_{\max} \ll N$. In some cases, it suffices to choose $l_{\max} = 2$ or $l_{\max} = 3$. Although Eq. (I.30) applies in principle to any electronic excited state n' , virtually all applications to be considered later involve the ground state $n' = 0$.

D. Model Potential Functions: Simple Particles

Direct solution of the electronic Schrödinger equation is a formidable task even for small numbers of electrons and nuclei, let alone for the very large numbers of both that are present in extended condensed phases. Although a wide variety of approximate solution methods for the underlying quantum problem exists [Parr, 1963; Torrens, 1972], these methods can be computationally demanding, their results may suffer from uncontrolled errors, and they may by themselves be uninformative from the standpoint of analytical statistical mechanics. This situation creates legitimacy for the introduction of model potential energy functions that mimic in at least some respects the experimental and quantum-computational information known about systems of interest. The basic desirable features of such models are conceptual clarity and mathematical simplicity. In addition, they can frequently offer computational speed advantage for numerical simulation when large numbers of particles are involved. The illustrative examples discussed in this and in Section I.E include specific cases as well as generic families of model potentials. They have been selected for a variety of reasons. Some have been widely used, some have unusual mathematical features, and some have been included to illustrate the wide variety of substances that can be described at least approximately by relatively simple modeling. These examples are all intended to represent qualitatively the electronic ground state potential energy “landscapes” for nuclear motion (i.e., $n' = 0$).

The cases discussed in this section all involve structureless, spherically symmetrical particles that (aside from possible external forces) by assumption engage only in pairwise additive interac-

tions. The following section (Section I.E) extends the discussion to include more complex particles with internal degrees of freedom, such as polyatomic molecules and cases requiring nonpairwise interactions. It should be kept in mind for all of these illustrations that model potentials need not, and typically do not, adhere strictly to all of the attributes mentioned in Section I.C. Nevertheless, their virtue is in representing some selected nontrivial many-body phenomena, without the “baggage” of distracting complication.

(1) INVERSE-POWER POTENTIALS

A particularly simple and transparent family of model many-particle potential energy functions consists of a sum of pair terms that are inverse powers of scalar distances. If only a single particle species is present, this model involves a potential energy function of the following form:

$$\Phi(\mathbf{r}_1 \dots \mathbf{r}_N) = \varepsilon \sum_{i < j} (\sigma/r_{ij})^{\bar{n}}, \quad (\text{I.31})$$

where the sum includes all pairs of particles that are present. Here, ε and σ are positive parameters with units of energy and length, respectively, which establish the scales for those basic properties. When this inverse-power form is applied to three-dimensional modeling, the exponent \bar{n} must obey the inequality $\bar{n} > 3$ in order to ensure that Φ is an extensive quantity [attribute (7) in Section I.C]. This case focuses attention exclusively on the strong repulsive forces that atoms or molecules experience when their electron clouds overlap, as when the many-particle system is subject to high external pressure, or when high-energy particle collisions are a dominant kinetic feature.

For a macroscopic collection of particles at fixed density, interacting according to this inverse-power potential, the configuration producing the absolute minimum value of Φ is a periodic face-centered cubic crystal structure [Dubin and Dewitt, 1994]; see Chapter IV. However, this is not the only mechanically stable arrangement (inherent structure) for the particles. In particular, the body-centered cubic lattice is also a local Φ minimum, though lying higher in energy for all $\bar{n} > 3$.

The fact that expression (I.31) is a homogeneous function of coordinates with degree $-\bar{n}$ has an obvious but mathematically useful consequence. Assume that periodic boundary conditions apply and that the N -particle system, initially confined to a region with volume V , has all of its coordinates scaled by a common factor $\zeta > 0$:

$$\mathbf{r}_1 \dots \mathbf{r}_N \rightarrow \zeta \mathbf{r}_1 \dots \zeta \mathbf{r}_N. \quad (\text{I.32})$$

The volume then becomes $\zeta^3 V$, and the initial potential energy $\Phi(\mathbf{r}_1 \dots \zeta \mathbf{r}_N)$ changes by a factor $\zeta^{-\bar{n}}$. In addition, this transformation has the property that any N -particle configuration that initially was a local Φ minimum (inherent structure) remains a local Φ minimum after scaling; and a similar remark applies to Φ extrema of other types (saddle points and maxima, if any). In particular, the number of mechanically stable potential energy minima, and their relative ordering in energy, are both invariant to the scaling. The same is true for the saddle points of Φ of various orders.

As exponent \bar{n} increases, the repelling pair interactions become steeper and steeper. The infinite- \bar{n} limit in Eq. (I.31) consequently produces the venerable hard-sphere model, a staple of

statistical mechanical theory [Hill, 1956; McQuarrie, 1976; Hansen and McDonald, 1986]. Length parameter σ then plays the role of the collision diameter for the hard spheres. Specifically, one has

$$\lim_{\bar{n} \rightarrow \infty} \Phi(\mathbf{r}_1 \dots \mathbf{r}_N) = \sum_{i < j} v_{hs}(r_{ij}), \quad (\text{I.33})$$

where

$$\begin{aligned} v_{hs}(r) &= +\infty & (r \leq \sigma), \\ &= 0 & (\sigma < r). \end{aligned} \quad (\text{I.34})$$

Because of the singular nature of the limit operation, ε does not explicitly appear in this result but nevertheless still manages formally to confer the dimension of energy on $v_{hs}(r)$.

Pairwise additive inverse power potentials for finite \bar{n} (often called “soft core models”) have provided the basis for several published studies of both crystal-phase and dense fluid-phase properties [Hoover, Young, and Grover, 1972; Martin and Singer, 1991; Vieira and Lacks, 2003].

(2) LENNARD-JONES 12,6 POTENTIAL

The Lennard-Jones pair potential model was originally proposed [Jones, 1924] to approximate the interactions between neutral particles in the gas phase, including both attractive and repulsive forces. It is most appropriately viewed as representing the electronic ground states of the noble gases helium, neon, argon, krypton, and xenon. Once again, single-atom interactions that might be caused by boundary confinement are put aside, and this model also truncates the identity (I.30) at just the atom pair level. Specifically, it postulates the following form for the total potential energy experienced by N atoms, all of the same species:

$$\Phi(\mathbf{r}_1 \dots \mathbf{r}_N | 0) = \varepsilon \sum_{i < j} v_{LJ}(r_{ij}/\sigma) \quad (\varepsilon, \sigma > 0), \quad (\text{I.35})$$

where again the sum includes all particle pairs, r_{ij} is the scalar distance between particles i and j , and $v_{LJ}(x)$ is a unit-depth reduced interaction defined as follows for $x > 0$:

$$v_{LJ}(x) = C(\bar{n}, \bar{m})(x^{-\bar{n}} - x^{-\bar{m}}) \quad (\bar{n} > \bar{m} > 3), \quad (\text{I.36})$$

$$C(\bar{n}, \bar{m}) = \left(\frac{\bar{n}}{\bar{m}} \right)^{\bar{m}/(\bar{n}-\bar{m})} \left(\frac{\bar{n}}{\bar{n}-\bar{m}} \right).$$

This equation constitutes an obvious extension of the preceding inverse-power pair potential. Although exponents \bar{n} and \bar{m} were originally treated as adjustable [Jones, 1924], it has become traditional more recently to refer to the “Lennard-Jones model” as specifically involving the choice $\bar{n}, \bar{m} = 12, 6$:

$$v_{LJ}(x) = 4(x^{-12} - x^{-6}). \quad (\text{I.37})$$

The positive parameters ε and σ , respectively, once again set the energy and length scales for the pair interactions, as appropriate for the specific substance of interest. The x^{-12} term produces strong interparticle repulsion at small separation, whereas the attractive x^{-6} term dominates at

large separation and possesses the correct distance dependence expected for long-range (nonrelativistic) dispersion interactions [Atkins, 1970]. It should be noted in passing that the Hellmann-Feynman relation (I.19) requires that neutral particles participating in attractive dispersion attractions at moderate to large distance from one another must at the same time display distortions of their isolated-particle electron distributions to be electrostatically consistent with those attractions.

The reduced Lennard-Jones 12,6 pair potential $v_{LJ}(x)$ in Eq. (I.37) has a single zero (at $x = 1$), and a single minimum (at $x = x_{\min} = 2^{1/6} \cong 1.1225$), for positive x :

$$v_{LJ}(1) = 0, \quad (\text{I.38})$$

$$v_{LJ}(x_{\min}) = -1.$$

The curvature at x_{\min} is the following:

$$v_{LJ}''(x_{\min}) = 72 \cdot 2^{-1/3} \cong 57.146. \quad (\text{I.39})$$

Furthermore, this function possesses a single inflection point at

$$x_{\text{infl}} = (26/7)^{1/6} \cong 1.2445, \quad (\text{I.40})$$

$$v_{LJ}(x_{\text{infl}}) = -133/169 \cong -0.78698.$$

By optimizing fits to experimental gas-phase data of simple substances, numerical values can be assigned to the Lennard-Jones scale parameters ϵ and σ . Measured equation of state virial coefficients, or alternatively measured viscosities, provide the type of input required. Table I.2 contains values that have been suggested as appropriate for the noble gases [Hirschfelder, Curtiss, and Bird, 1954]. Both parameters increase steadily with increasing atomic number Z because of the growing number of electrons bound in the neutral atoms. The result is increased overlap repulsion at small separation and stronger dispersion attraction at large separation.

The scientific literature contains a large number of publications in which the pairwise-additive Lennard-Jones 12,6 potential plays a central role. Representative examples of those publications can be cited in which this model potential has been used to represent gas-phase clusters [Wales and Berry, 1990; Tsai and Jordan, 1993b], the liquid state [Hansen and McDonald, 1986; Malandro and Lacks, 1998], crystalline solids [Somasi et al., 2000; Stillingner, 2001], and amorphous solids [Fox and Andersen, 1984; Vollmayr et al., 1996], thus approximating each of these states exhibited by the heavier noble gases. The special cases of the light helium isotopes involving

TABLE I.2. Energy and length scale parameters for the noble gases represented by the Lennard-Jones 12,6 pair potential^a

Species	He	Ne	Ar	Kr	Xe
Atomic no. (Z)	2	10	18	36	54
$\epsilon/k_B, \text{K}$	10.22	35.60	119.8	171	221
σ, nm	0.2556	0.2749	0.3405	0.360	0.410

^aTaken from Hirschfelder, Curtiss, and Bird, 1954, p. 1110.

strong atomic quantum effects also incorporate Lennard-Jones-like interactions but require separate discussion, which is presented in Chapter VIII.

When mixtures of different substances are present, several distinct pairs of Lennard-Jones energy and length scale parameters are required. It can then be impractical to determine all such pairs experimentally. In that situation, it has been traditional to invoke empirical combining rules that use the parameters for the pure substances. For two species a and b , the cross-species Lennard-Jones energy and length parameters conventionally are set equal respectively to the geometric and arithmetic means of those for the pure substances [Hirschfelder, Curtiss, and Bird, 1954, p. 168]:

$$\varepsilon_{ab} = (\varepsilon_{aa} \varepsilon_{bb})^{1/2}, \quad (\text{I.41})$$

$$\sigma_{ab} = (\sigma_{aa} + \sigma_{bb})/2.$$

(3) MORSE POTENTIAL

The Lennard-Jones 12,6 pair potential contains only two adjustable parameters, fixing energy and length scales. For some applications, it is desirable to have greater functional flexibility. The Morse pair potential offers three adjustable parameters (ε , σ , r_e) [Morse, 1929]. It has the following parameterized form:

$$\varepsilon v_M[(r - r_e)/\sigma], \quad (\text{I.42})$$

where

$$v_M(x) = \exp(-2x) - 2 \exp(-x). \quad (\text{I.43})$$

As was the case with the Lennard-Jones pair potential, ε denotes the depth of the Morse potential at its single minimum, and σ controls its length scale. The position of the minimum (i.e., the mechanical equilibrium pair distance) is independently set by r_e . Although v_M has neither the capacity to produce a divergence at small pair separation nor a long-range dispersion attraction varying as r^{-6} , these attributes may be inconsequential for some applications.

The properties of v_M to be compared with those shown in Eqs. (I.38)–(I.40) for v_{LJ} are as follows ($x_{\min} = 0$):

$$v_M(-\ln 2) = 0, \quad (\text{I.44})$$

$$v_M(x_{\min}) = -1;$$

$$v_M''(x_{\min}) = 2; \quad (\text{I.45})$$

$$x_{\text{infl}} = \ln 2, \quad (\text{I.46})$$

$$v_M(x_{\text{infl}}) = -3/4.$$

One obvious advantage of v_M over v_{LJ} is its ability to provide via σ independent control of the curvature at the minimum of the rescaled pair potential (I.42) for fixed equilibrium pair bond length r_e and depth ε .

In the large- N limit, a many-body potential energy function composed of Morse pair interactions, to describe an electronic ground-state situation,

$$\Phi(\mathbf{r}_1 \dots \mathbf{r}_N | 0) = \varepsilon \sum_{i < j} v_M[(r_{ij} - r_e)/\sigma], \quad (\text{I.47})$$

must conform to the lower-bound criterion stated in Eq. (I.29). This criterion places a constraint on the acceptable values of r_e and σ . If the N particles are arranged so that essentially equal subsets of $N/4$ are placed precisely on top of one another at the vertices of a regular tetrahedron with sides equal to r_e , then the requirement that Φ be bounded below by $-KN$, $K > 0$, leads to the inequality

$$\exp(r_e/\sigma) \geq 3. \quad (\text{I.48})$$

(4) GAUSSIAN CORE MODEL POTENTIAL

Several unusual mathematical properties create an intrinsic interest in the model potential energy function consisting of a pairwise sum of suitably scaled Gaussian terms:

$$\Phi(\mathbf{r}_1 \dots \mathbf{r}_N) = \varepsilon \sum_{i < j} \exp[-(r_{ij}/\sigma)^2] \quad (\varepsilon, \sigma > 0). \quad (\text{I.49})$$

Historically, this form could be viewed as originating in polymer solution theory, where the individual Gaussian terms approximated interactions between randomly coiling linear polymers [Flory, 1953]; see Chapter X. However, the simple form in Eq. (I.49) is best interpreted as corresponding to structureless, spherically symmetric “soft” particles.

In its remote tail region, each Gaussian pair interaction approaches zero more and more rapidly in relative terms as r increases. This attribute is measured by the logarithmic rate of change quantity

$$d \ln \{ \varepsilon \exp[-(r/\sigma)^2] / dr = -2r/\sigma^2, \quad (\text{I.50})$$

indicating that the relative steepness increases in direct proportion to the separation r . Of course, the pair interaction itself is very small at large r . But if two Gaussian core particles (in isolation from all others), initially widely separated, approach one another with very low relative kinetic energy E , they experience virtually a rigid sphere collision at an effective collision diameter:

$$r_{coll}(E) \approx \sigma [\ln(\varepsilon/E)]^{1/2}. \quad (\text{I.51})$$

This observation underlies the low-temperature, low-density asymptotic reduction of the Gaussian core model to the hard-sphere model discussed in Eqs. (I.33)–(I.34) [Stillinger and Stillinger, 1997].

The spatial arrangement of Gaussian core particles in a macroscopic system that attains the minimum potential energy is a face-centered cubic lattice at low density but a body-centered cubic arrangement at high density [Stillinger, 1976]. The corresponding lattice energies Φ_{fcc} and Φ_{bcc} obey an exact duality relation [Stillinger, 1979; Stillinger and Stillinger, 1997]. To exhibit this connection, define

$$I_{fcc}(\rho) = \varepsilon + \lim_{N \rightarrow \infty} [2\Phi_{fcc}(\rho)/N], \quad (\text{I.52})$$

$$I_{bcc}(\rho') = \varepsilon + \lim_{N \rightarrow \infty} [2\Phi_{bcc}(\rho')/N],$$

where ρ and ρ' are the respective values of the particle number density N/V . If these number densities satisfy the following identity:

$$\rho\rho' = \pi^{-3}\sigma^{-6}, \quad (\text{I.53})$$

then it follows from the self-similarity of the Gaussian function under Fourier transformation that

$$(\rho)^{-1/2}I_{fcc}(\rho) = (\rho')^{-1/2}I_{bcc}(\rho'). \quad (\text{I.54})$$

This duality relation has the useful property that lattice energy at high density, where many neighbors interact, can be reduced to evaluation of a low-density lattice energy, where few neighbors are close enough to interact to a significant extent. The lattice energies per particle for the two structures are equal at the self-dual density $\rho\sigma^3 = \rho'\sigma'^3 = \pi^{-3/2}$.

Let $f(\mathbf{R})$ be a function defined in the $3N$ -dimensional configuration space $\mathbf{R} \equiv \mathbf{r}_1 \dots \mathbf{r}_N$, and let $\mathbf{L}(\lambda)$ be a convolution operator that entails smoothing over this space with a Gaussian kernel possessing width λ :

$$\mathbf{L}(\lambda)*f(\mathbf{R}) = (\pi^{1/2}\lambda)^{-3N} \int \exp[-(\mathbf{R} - \mathbf{R}')^2/\lambda^2] f(\mathbf{R}') d\mathbf{R}'. \quad (\text{I.55})$$

In particular, applying this operator to a Gaussian function results in another Gaussian function with increased width but with a diminished maximum value. For the N -particle potential energy function in Eq. (I.49) consisting of a sum of Gaussians, one finds [Stillinger and Stillinger, 1997]:

$$\Phi[\mathbf{R}/(1 + \delta)] = (1 + \delta)^3 \mathbf{L}\{[(\delta^2/2) + \delta]^{1/2}\sigma\}*\Phi(\mathbf{R}), \quad \delta \geq 0. \quad (\text{I.56})$$

Consequently, shrinking all particle coordinates by factor $(1 + \delta)^{-1}$, or equivalently increasing the number density by factor $(1 + \delta)^3$, is equivalent to applying both the smoothing operator and a magnitude renormalization to Φ . In view of the fact that smoothing tends to eliminate maxima and minima, though the absolute minimum of the Gaussian core model potential at high density is the body-centered cubic lattice, this lattice evidently is the only mechanically stable structure that survives in the asymptotic high-density limit.

(5) YUKAWA POTENTIAL

Another frequently cited pair interaction is the Yukawa potential. For a single-component many-body system, the potential energy function (exclusive of single-particle terms $v^{(1)}$) has the form

$$\Phi(\mathbf{r}_1 \dots \mathbf{r}_N) = \varepsilon \sum_{i < j} v_Y(r_{ij}/\sigma), \quad (\text{I.57})$$

where

$$v_Y(x) = \exp(-x)/x. \quad (\text{I.58})$$

This elementary function retains the name attributable historically to its appearance in the early theory of meson-mediated nucleon interactions [Yukawa, 1935]. More relevant to the general subject currently under consideration is that it has the form of a shielded Coulomb pair interaction, as appears in Debye-Hückel electrolyte theory [Debye and Hückel, 1923; also see Section V.G

in Chapter V]. In order for the potential to satisfy the global stability criterion (I.29), the energy scaling parameter ε cannot be negative.

(6) COLLECTIVE DENSITY VARIABLE REPRESENTATION

In the event that the potential energy function Φ consists only of a sum of spherically symmetric pair interactions for identical particles, an alternative representation of that function may be available that is based on collective density variables. For some purposes, this alternative offers conceptual and mathematical advantages.

Let the particle system be contained within a rectangular solid region with linear dimensions L_x, L_y, L_z , and volume $V = L_x L_y L_z$, and furthermore assume that periodic boundary conditions apply to this region. This geometry allows introduction of an infinite set of wave vectors \mathbf{k} , each one of which has Cartesian components:

$$\mathbf{k} = (2\pi m_x/L_x, 2\pi m_y/L_y, 2\pi m_z/L_z), \quad (\text{I.59})$$

$$m_x, m_y, m_z = 0, \pm 1, \pm 2, \dots$$

Collective density variables $\rho(\mathbf{k})$ are then defined for each wave vector by sums over all particle positions \mathbf{r}_j within V :

$$\rho(\mathbf{k}) = \sum_{j=1}^N \exp(i\mathbf{k} \cdot \mathbf{r}_j). \quad (\text{I.60})$$

As a result of this definition, one has the following obvious properties:

$$\rho^*(\mathbf{k}) = \rho(-\mathbf{k}),$$

$$\rho(0) = N, \quad (\text{I.61})$$

$$0 \leq |\rho(\mathbf{k})| \leq N \quad (\mathbf{k} \neq 0).$$

The spherically symmetric pair potential acting between particles is denoted by $v^{(2)}(r)$, i.e.:

$$\Phi = \sum_{j < l} v^{(2)}(r_{jl}). \quad (\text{I.62})$$

Assuming that it exists, the Fourier transform of $v^{(2)}(r)$, defined for the wave vector set (I.59), involves an integral over the finite system volume V :

$$V^{(2)}(\mathbf{k}) = \int_V v^{(2)}(r) \exp(i\mathbf{k} \cdot \mathbf{r}) d\mathbf{r}. \quad (\text{I.63})$$

The inverse transform requires a sum over all instances of \mathbf{k} :

$$v^{(2)}(r) = V^{-1} \sum_{\mathbf{k}} V^{(2)}(\mathbf{k}) \exp(-i\mathbf{k} \cdot \mathbf{r}). \quad (\text{I.64})$$

Each pair potential term in the right side of Eq. (I.62) may be replaced by this last inverse transform sum, with the result

$$\begin{aligned} \Phi &= V^{-1} \sum_{j < l} \sum_{\mathbf{k}} V^{(2)}(\mathbf{k}) \exp[-i\mathbf{k} \cdot (\mathbf{r}_j - \mathbf{r}_l)] \\ &= (2V)^{-1} \sum_{j \neq l=1}^N \sum_{\mathbf{k}} V^{(2)}(\mathbf{k}) \exp[-i\mathbf{k} \cdot (\mathbf{r}_j - \mathbf{r}_l)] \end{aligned}$$

$$\begin{aligned}
 &= (2V)^{-1} \sum_{\mathbf{k}} V^{(2)}(\mathbf{k}) \left\{ \sum_{j,l=1}^N \exp[-i\mathbf{k} \cdot (\mathbf{r}_j - \mathbf{r}_l)] - N \right\} \\
 &= (2V)^{-1} \sum_{\mathbf{k}} V^{(2)}(\mathbf{k}) [\rho(\mathbf{k})\rho(-\mathbf{k}) - N].
 \end{aligned} \tag{I.65}$$

Although this set of equations formally expresses the total potential as a quadratic form in the collective density variables, it is important to keep in mind that these variables are not independent, and as a result they are subject to complicated nonlinear constraints [Fan et al., 1991; Uche et al., 2004].

The Fourier transform $V^{(2)}(\mathbf{k})$ does not exist for the Lennard-Jones pair potentials, Eqs. (I.36)–(I.37). However, it does exist for the more shape-flexible Morse potential, Eqs. (I.42)–(I.43). In the limit where the linear dimensions of the system volume V far exceed the range of that pair function, one has

$$\begin{aligned}
 V^{(2)}(\mathbf{k}) &= \varepsilon \int_{V_M} [(r - r_e)/\sigma] \exp(i\mathbf{k} \cdot \mathbf{r}) d\mathbf{r} \\
 &= 16\pi\varepsilon\sigma^3 \left[\frac{\exp(2r_e/\sigma)}{(4 + \sigma^2 k^2)^2} - \frac{\exp(r_e/\sigma)}{(1 + \sigma^2 k^2)^2} \right].
 \end{aligned} \tag{I.66}$$

Another case of interest involves a repelling Gaussian pair potential that generates the Gaussian core model mentioned above [Stillinger and Stillinger, 1997]. This is one of the simplest circumstances in which the pair potential and its Fourier transform are self-similar:

$$v^{(2)}(r) = \varepsilon \exp[-(r/\sigma)^2]; \tag{I.67}$$

$$V^{(2)}(\mathbf{k}) = \pi^{3/2} \varepsilon \sigma^3 \exp(-\sigma^2 k^2/4), \tag{I.68}$$

a property that underlies the duality identities for this model mentioned above, Eqs. (I.52)–(I.53). Finally note that the Yukawa pair potential $\varepsilon v_Y(r/\sigma)$ has the following Fourier transform:

$$V^{(2)}(k) = \frac{4\pi\varepsilon\sigma^3}{1 + \sigma^2 k^2}, \tag{I.69}$$

exhibiting a long algebraic falloff with increasing k because of the coulombic divergence of the potential at the origin in \mathbf{r} space.

An unusual feature can arise if the pair potential $v^{(2)}(r)$ has a non-negative Fourier transform that vanishes identically beyond some radius in \mathbf{k} space:

$$\begin{aligned}
 V^{(2)}(\mathbf{k}) &> 0 \quad (0 \leq |\mathbf{k}| \leq K) \\
 &= 0 \quad (K < |\mathbf{k}|).
 \end{aligned} \tag{I.70}$$

If K is sufficiently small that fewer than $3N$ wave vectors \mathbf{k} fall within that radius about the origin, then the absolute minimum for Φ is attained by having all of the corresponding $|\rho(\mathbf{k})| = 0$. However, this condition does not exhaust all of the system's degrees of freedom. Consequently, the absolute Φ minimum remains configurationally highly degenerate, and for small enough K this situation can produce amorphous classical ground states in which the N particles are free to reconfigure along a large set of configuration space pathways [Uche et al., 2006].

E. Model Potential Functions: Complex Particles

(1) SATURATING CHEMICAL BONDS

The behavior of a wide range of chemical substances involves formation and dissociation of strong chemical bonds between the constituent atoms. Obvious examples include monovalent elements that tend to be present as diatomic molecules, such as hydrogen (H_2), oxygen (O_2), nitrogen (N_2), and chlorine (Cl_2). Elemental sulfur (S) is divalent and consequently forms closed polygons or chains of bonded atoms [Donohue, 1982]. Silicon (Si) is tetravalent, forming at low temperature a diamond-structure crystal with local chemical bonding geometry that connects each atom to four equivalent neighbors located at the vertices of a surrounding regular tetrahedron. These chemically preferred valences, and the local patterns of bond angles at each participating atom, cannot be described accurately in terms of spherically symmetric pair interactions $v^{(2)}(r_{ij})$ alone. However, at least a rudimentary description of chemical valency in the electronic ground state can be achieved by combining pair potentials with a proper choice of three-atom functions $v^{(3)}(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k)$:

$$\Phi(\mathbf{r}_1 \dots \mathbf{r}_N | 0) \cong \sum_{i < j} v^{(2)}(r_{ij}) + \sum_{i < j < k} v^{(3)}(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k). \quad (I.71)$$

Here the role of the pair terms $v^{(2)}$ is to create chemical bonds individually with appropriate strength and length scales. The atom-triplet terms $v^{(3)}$ can then be chosen to discourage formation of more than the number of chemical bonds allowed by the valence of the element under consideration and to establish the preferred angles between bonds at any atom when the valence of that atom is 2 or greater.

One example suffices to illustrate the fixed-valency concept. This example involves the ground electronic state for elemental fluorine (F), which is monovalent and which consequently can exist as a covalently bonded diatomic molecule, F_2 . A combination of two-atom and three-atom interactions of the type in Eq. (I.71) has been constructed and used in computer simulation [Harris and Stillinger, 1990]. In the interests of computational simplicity, both the two-atom and three-atom interactions were taken to vanish identically beyond a modest distance range on the molecular scale. The pair function was chosen to be

$$v^{(2)}(r) = \varepsilon_{FF} u^{(2)}(r/\sigma_{FF}), \quad (I.72)$$

in which

$$\varepsilon_{FF} = 160.2263 \text{ kJ/mol}, \quad (I.73)$$

$$\sigma_{FF} = 0.12141 \text{ nm},$$

and

$$u^{(2)}(x) = A(x^{-8} - x^{-4})E(x - 3.6). \quad (I.74)$$

Here the function $E(y)$ has the following definition:

$$\begin{aligned} E(y) &= \exp(y^{-1}) & (y < 0), \\ &= 0 & (y \geq 0), \end{aligned} \quad (I.75)$$

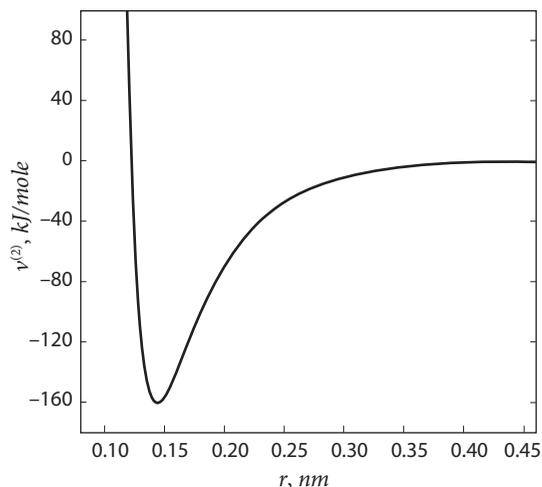


FIGURE I.2. Model pair potential for elemental fluorine, Eq. (I.72) [Harris and Stillinger, 1990].

so that $E(y)$ is continuous and has continuous derivatives of all orders for all real y . The dimensionless constant A was set equal to 6.052 463 017 so that $u^{(2)}(x)$ possesses a unit-depth minimum. With these choices, the implied equilibrium bond length for the isolated F_2 molecule is 0.1435 nm, the harmonic vibrational frequency is 896.9 cm^{-1} , and the dissociation energy is 160.2263 kJ/mol, all close to the corresponding spectroscopically measured values (0.1435 nm, 892 cm^{-1} [Herzberg, 1950], and 160.0508 kJ/mol [Huber and Herzberg, 1979]). The pair potential presented in Eq. (I.72), as well as all its distance derivatives, continuously approach zero and remain vanishing, as r increases to and exceeds the cutoff distance 0.437 076 nm. Figure I.2 shows a plot of this fluorine pair potential.

Besides enforcing the monovalency of the model fluorine atoms, the three-body contributions $v^{(3)}$ can be chosen to yield a moderately realistic description of the chemical exchange reaction $F + F_2 \rightarrow F_2 + F$, avoiding the pitfall of too large a transition-state barrier. A choice matched to the above pair potential in Eq. (I.72) has the following form that is necessarily symmetrical under atom permutations [Harris and Stillinger, 1990]:

$$v^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = \varepsilon_{FF} [f(r_{12}/\sigma_{FF}, r_{13}/\sigma_{FF}, \theta_1) + f(r_{12}/\sigma_{FF}, r_{23}/\sigma_{FF}, \theta_2) + f(r_{13}/\sigma_{FF}, r_{23}/\sigma_{FF}, \theta_3)], \quad (\text{I.76})$$

where $0 \leq \theta_i \leq \pi$ is the triangle vertex angle at nucleus i , and

$$f(x, y, \theta) = 8.4(xy)^{-4}E(x - 3.6)E(y - 3.6) + (55 - 25 \cos^2 \theta)E[(x - 2.80)/3]E[(y - 2.80)/3]. \quad (\text{I.77})$$

With these two-body and three-body interaction choices, the transition state for three fluorine atoms is a symmetric linear arrangement, and at that state the potential energy possesses negative curvature along the direction of asymmetric stretch, the reaction coordinate. Figure I.3 presents a

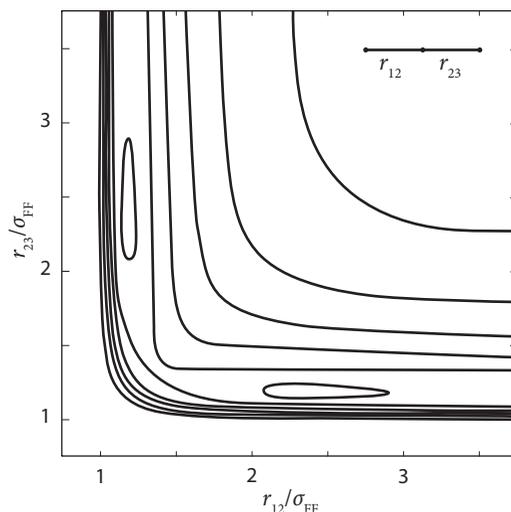


FIGURE I.3. Contour plot of the reduced potential energy for three fluorine atoms in a linear arrangement, shown vs. reduced distances. The two asymmetric minima occur within the closed contours at which the reduced energy $\Phi/\epsilon_{FF} = -1.01$. Contours of successively increasing energy, moving outward from the minima, are at reduced energies $-1.01, -0.85, -0.70, -0.50, -0.30$, and -0.10 .

contour plot of this model's potential energy for three atoms in the linear-configuration subspace containing the transition state. An equivalent pair of asymmetrical minima occur at $r_{12}/\sigma_{FF} = 1.1887$, $r_{23}/\sigma_{FF} = 2.3322$ and the reverse, at which the reduced interaction energy is $\Phi/\epsilon_{FF} = -1.03895$. The symmetrical transition state at $r_{12}/\sigma_{FF} = r_{23}/\sigma_{FF} = 1.3649$ has $\Phi/\epsilon_{FF} = -0.85997$, which is 28.677 kJ/mol above the minima.

Analogously structured combinations of two-atom and three-atom interaction functions can be selected to describe substances exhibiting higher valence chemical bonding. Divalent elemental sulfur (S) has been modeled in this manner in order to simulate temperature effects in its liquid phase [Stillinger, Weber, and LaViolette, 1986; Stillinger and Weber, 1987]. The divalency of this element is known experimentally to lead to preferred angles between bonds at an atom and thus to formation of octameric molecular rings (S_8) at low temperature (specifically below the melting temperature at low pressure). But this divalency also leads to rings of other sizes containing both even and odd numbers of atoms and to long linear polymers at elevated temperature [MacKnight and Tobolsky, 1965; Steudel, 1984].

The same kinds of two-atom plus three-atom model potentials have also been constructed to describe and to simulate the tetravalent semiconductors silicon (Si) [Stillinger and Weber, 1985a; Biswas and Hamann, 1987] and germanium (Ge) [Ding and Andersen, 1986]. As was the case for the monovalency and divalency cases just mentioned, the role of the three-body nonadditive interactions is to cause saturation of chemical bond formation and to control the angles between bonds simultaneously impinging on any given atom.

It should be noted in passing that whenever three-body interactions are present, the number of terms to be considered in a large N -atom system nominally requires arduous triple summation over all particles. However, if the $v^{(3)}$'s have the forms shown in Eq. (I.76), with f 's that are products of radial functions and polynomials in angle sines and cosines as in Eq. (I.77), then in certain

cases it is possible to reduce triple sums to double sums [Biswas and Hamann, 1987; Weber and Stillinger, 1993]. Such reductions can substantially speed up computer calculations based on that class of models.

(2) INTACT MOLECULES

Many applications in the study of condensed-matter phenomena concern neutral molecules or polyatomic ions whose chemical structures remain stable in the physical circumstances of interest (temperature, pressure, irreversible flows). Nuclei continue to be chemically bonded within the same molecular or ionic groupings throughout the observation “time window.” For these applications, it is unnecessary, even undesirable, to consider the entire Born-Oppenheimer potential energy hypersurface throughout its full configuration space. Instead, the relevant chemical subspace of the full configuration space is identified, and model potential functions are then generated for just that subspace. In doing so, the model functions should be chosen to ensure that the desired chemical bonding patterns cannot be violated by chance nuclear excursions. In these circumstances, it is natural to subtract the intramolecular ground-state minimum energies for the molecules or ions from Φ , which then measures only the combination of internal distortion energies of the stable molecules or ions, the potentials of interaction they have with any walls present, and the interactions between neighboring intact molecules or ions.

Water offers a representative and obviously important example. Its condensed-phase properties and their molecular interpretations form the subject of Chapter IX. A system comprising N oxygen nuclei and $2N$ hydrogen nuclei, in the presence of $10N$ electrons so as to be electrostatically neutral overall, can form N H_2O molecules. The Born-Oppenheimer electronic ground state for one such molecule has C_{2v} symmetry at its own potential energy minimum, with a structure illustrated in Figure I.4. The dipole moment for the molecule in isolation points along the direction of the symmetry axis and has magnitude (in Debye) 1.855 D [Dyke and Muentzer, 1973]. Its three vibrational normal modes (with light hydrogens ^1H) have frequencies equal to $3,656.65\text{ cm}^{-1}$ (symmetric stretch), $3,755.79\text{ cm}^{-1}$ (asymmetric stretch), and $1,594.59\text{ cm}^{-1}$ (symmetric bend)

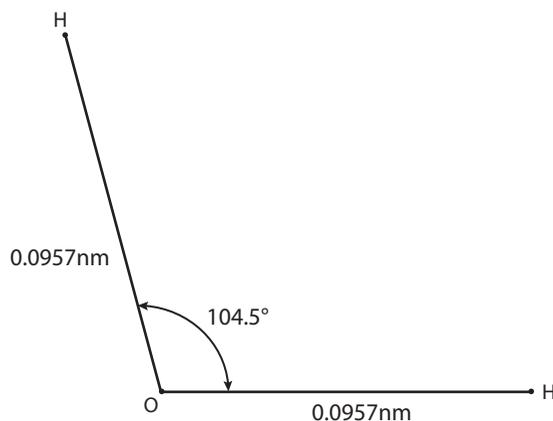


FIGURE I.4. Ground-state structure of the water molecule [Eisenberg and Kauzmann, 1969].

[Eisenberg and Kauzmann, 1969, p. 7]. Needless to say, each of these mode frequencies decline upon isotopic substitution of the light hydrogens by heavier deuterium.

Water molecules are internally quite stiff, i.e., their internal restoring forces resisting bond bending and bond stretching are quite large, as indicated by the cited mode frequencies. Consequently in liquid water at room temperature and pressure or in ice at lower temperature and similar pressure the molecules retain nearly their isolated-molecule structure. Furthermore, only about 5 molecules in 10^8 are found to have dissociated into solvated H^+ and OH^- ions in the room-temperature liquid [Eisenberg and Kauzmann, 1969, Table 4.9], although this fraction rises considerably with increasing temperature and pressure [Tödheide, 1972]. As a result, it is reasonable to construct and exploit water models that postulate permanently intact molecules and that do not involve exchange of atoms between those molecules. Chapter IX discusses several such cases. Without any restriction to permanently intact H_2O molecules, the full Born-Oppenheimer potential function Φ for N oxygens and $2N$ hydrogens would have each of its geometrically distinct mechanically stable minima (inherent structures) belonging to a set of $N!(2N)!$ permutation-equivalent inherent structures. However, the intact-molecule restraint reduces this equivalence number to the much smaller value $N!2^N$ because then the N molecules can be permuted among themselves, but each of the N molecules has only two equivalent configurations that differ by intramolecular hydrogen exchange through rotation by angle π about its symmetry axis.

The generalization of this reduction in number of geometrically equivalent inherent structures is straightforward when considering stiff-molecule or stiff-ion models for other substances. Consider the case of N molecules, each of which contains $\nu(i)$ atoms of species i . Therefore, the system of interest has the corresponding composition: precisely $\nu(i)N$ atoms for each of the species i . Then without the restriction to permanently intact stiff molecules, each Φ inherent structure would belong to an equivalence set comprising

$$\prod_i [\nu(i)N]! \quad (I.78)$$

members. By contrast, N permanently intact stiff molecules that each have symmetry number $\bar{\sigma}$ for reorientation among their own equivalent positions would be able to attain only

$$N!\bar{\sigma}^N \quad (I.79)$$

indistinguishable inherent structures on the multidimensional Φ landscape.

The potential energy function for intact molecules confined to their own portion of the full configuration space has a resolution into one, two, three, ..., N molecule contributions analogous to that exhibited in Eq. (I.30) for individual atoms. In the case of a single species, let \mathbf{y}_i stand for the collection of coordinates required to specify the location, orientation, and internal deformation of molecule i , $1 \leq i \leq N$. Then one has the following expression for the many-stable-molecule potential energy function (implicitly assumed to refer to the electronic ground state):

$$\Phi(\mathbf{y}_1 \dots \mathbf{y}_N) \equiv \sum_{i=1}^N v^{(1)}(\mathbf{y}_i) + \sum_{i=2}^N \sum_{j=1}^{i-1} v^{(2)}(\mathbf{y}_i, \mathbf{y}_j) + \sum_{i=3}^N \sum_{j=2}^{i-1} \sum_{k=1}^{i-1} v^{(3)}(\mathbf{y}_i, \mathbf{y}_j, \mathbf{y}_k) + \dots + v^{(N)}(\mathbf{y}_1 \dots \mathbf{y}_N) \quad (I.80)$$

where as before the individual $v^{(l)}$ functions, $1 \leq l \leq N$, are to be determined sequentially from interactions of increasing numbers of molecules. The generalization of this expression to the case of systems containing several intact molecular and/or ionic species is straightforward. The leading

contributions $v^{(1)}(\mathbf{y}_i)$ now contain intramolecular interactions for flexible molecules, as well as any external force contributions operating on the individual molecules.

(3) CHIRAL MOLECULE ENANTIOMERS

The tetrahedrally radiating pattern of four single covalent bonds emanating from a carbon atom is a rather rigid feature in a molecule. Under ambient temperature and pressure conditions, only minor angular displacements in this pattern would occur. If the four portions of the molecule attached to such a carbon atom by those covalent bonds are chemically distinguishable, then that carbon is identified as a “stereocenter.” This name implies that a molecule containing such a specific tetrahedral arrangement of the bonds to those four portions cannot be superimposed on its mirror-image molecule by any combination of translation and rotation. If only one stereocenter is present, then the molecule and its mirror image are distinguishable chiral species, called “enantiomers.” Figure I.5 illustrates this situation, generically labeling the four distinct attachments A_1 , A_2 , A_3 , A_4 . As an example, if these attachments are specifically chosen to be a hydrogen atom ($-H$), a fluorine atom ($-F$), a methyl group ($-CH_3$), and an ethyl group ($-CH_2-CH_3$), the result would be one of the two enantiomers of a 2-fluorobutane molecule. As is discussed in Chapter XI, the overwhelming majority of amino acids that form the building blocks of protein molecules in terrestrial living organisms are chiral species of just one enantiomer.

Enantiomers are experimentally easily distinguishable from one another because they are optically active, that is, they rotate the plane of transmitted polarized light in opposite directions. A mixture containing equal amounts of the two enantiomers is called a “racemic” mixture, and it has no net rotational effect on the plane of transmitted polarized light.

In principle, the full Born-Oppenheimer ground-state potential function Φ would not discriminate between enantiomers. In other words, when Φ displays an inherent structure minimum for one enantiomer of a chiral molecule, it must also exhibit an equivalent mirror-image inherent structure minimum for the other enantiomer. But for substances such as 2-fluorobutane and the

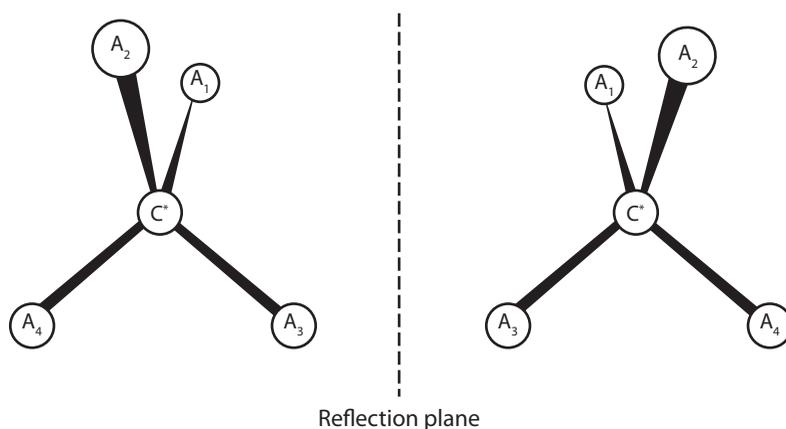


FIGURE I.5. Schematic illustration of the geometric structures of a chiral molecule and its mirror image, each of which contains a stereocenter carbon atom C^* . The four covalently attached structures denoted by A_1 , A_2 , A_3 , A_4 must be chemically distinguishable.

chiral amino acids, these inherent structures must be separated by high energy barriers in the Φ landscape. This is necessary to be consistent with the experimental fact that the enantiomers can be treated as distinct molecular species whose numbers remain unchanged over time if the ambient conditions are not extreme. This barrier height requirement would place restrictions on any approximation used for the intramolecular interaction portion of $v^{(1)}(\mathbf{y}_i)$ in Eq. (I.80).

(4) RIGID BOND LENGTHS

Because of the relative nondeformability of many small molecular species such as water, a useful level of simplification often invoked treats each molecule as a strictly rigid object with fixed bond lengths and in some cases fixed bond angles. This method reduces the relevant configuration space even further than as discussed in Section I.E(2). Rigid linear molecules [examples are diatomic nitrogen (N_2) and triatomic carbon dioxide (CO_2)] would then require only five configurational coordinates, the center position coordinates and two polar angles. Rigid nonlinear molecules [such as water (H_2O), and benzene (C_6H_6)] would require six configurational coordinates, the center position coordinates and three Euler angles, to specify spatial orientation [Goldstein, 1953].

Realistically modeling the interactions of some classes of intact but nonrigid molecules requires explicit inclusion of some internal conformational degrees of freedom. This is the case, for example, with the saturated linear hydrocarbons (normal alkanes) that have chemical compositions $\text{C}_n\text{H}_{2n+2}$ for $n \geq 4$. Even with fixed chemical bond lengths and fixed angles between vertex-sharing chemical bond pairs emanating from its carbon atoms, $n - 3$ dihedral angles are still needed to specify the conformation of the carbon-atom backbone chain of the alkane molecule, as well as two additional angles for rotation of its two terminal methyl groups ($-\text{CH}_3$). This process requires that a model potential energy function Φ for normal alkanes, even when simplified by the fixed-bond-length and fixed-bond-angle assumptions, must include within its single-molecule $v^{(1)}$ contributions at least a portion depending explicitly on those $n - 1$ remaining angles.

(5) FORCE CENTER ASSIGNMENTS

The interactions that actually operate in solid and fluid condensed phases of intact molecules may involve a substantial contribution from nonpair terms $v^{(j)}(j > 2)$ in Φ , when resolved as in Eq. (I.80) into one, two, three, ..., molecule portions. In particular, this is the case for collections of the polar, and polarizable, water molecules. It is also a significant issue when ions are present. The calculation of induced dipoles in a condensed-phase configuration involves solving $O(N)$ simultaneous linear equations, often an impractical computational situation. Consequently, these and other nonpair effects need to be incorporated at least approximately in any model that successfully represents these condensed-phase situations. One strategy to account for nonpair terms is to devise an “effective pair potential,” chosen to fit a set of measured properties for the substance of interest, then applied to the study of other properties [Stillinger, 1970; Stillinger et al., 2002]. Because the specific choice of fitting criteria would typically depend on an investigator’s special interests, and consequently vary from case to case, there can be no generally agreed upon “uniquely best” effective pair potential [see Box IX.1 for details]. However, this non-uniqueness does not invalidate the approach.

The most straightforward yet flexible strategy for creating an effective intermolecular pair potential involves use of an appropriately chosen number of spherically symmetric force centers within each molecule or ion. These centers are fixed with respect to local subsets of the nuclei and chemical bonds of each molecule and can interact with force centers attached to neighboring molecules via radial functions of the distance between those force centers. Consequently, the effective molecule–molecule pair interaction would have the following form:

$$v_{\text{eff}}^{(2)}(i, j) = \sum_{\eta} \sum_{\zeta} b_{\eta\zeta} (|\mathbf{R}_j + \mathbf{u}_{\eta} - \mathbf{R}_i - \mathbf{u}_{\zeta}|). \quad (\text{I.81})$$

In this expression, single “origin-center” locations embedded in each of molecules i and j have respectively been denoted by \mathbf{R}_i and \mathbf{R}_j . Indices η and ζ label the various force centers in i and j , with displacements \mathbf{u}_{η} and \mathbf{u}_{ζ} from \mathbf{R}_i and \mathbf{R}_j , respectively. The individual force centers in a molecule need not be located precisely at its nuclei nor be equal in number to those nuclei. The radial functions $b_{\eta\zeta}$ could then be chosen from a suitable function set to minimize error in prediction of a weighted sum of experimental properties for the molecular substance under consideration. Such selection should be carried out so as to satisfy, to the extent possible, the general mathematical properties of potential functions discussed in Section I.C. For some applications, the functional forms exhibited by the pair potentials described in Section I.D may serve as useful force-center interaction potentials for complex molecules [e.g., the Lennard-Jones 12,6 function, Eq. (I.37)].

Choosing $b_{\eta\zeta}$'s for homonuclear diatomic molecules such as oxygen (O_2), nitrogen (N_2), or chlorine (Cl_2) can rely on short-range functions because no molecular dipole moments are involved. Although the positions of the nuclei could serve as the force centers in the event that two centers per diatomic molecule are to be used, this may not be the optimal choice. It may be more appropriate to displace the force centers inward toward the molecular center. This would be consistent with the accumulation of electron density between the chemically bonded atoms, as described by the adapted Hellmann-Feynman theorem, Eq. (I.19).

Molecules containing nonequivalent nuclei, such as water, can have net electrostatic charges attributed to each of the constituent atoms and assigned in turn to the force centers. This concept justifies inclusion of long-range coulombic tails in the force-center functions:

$$b_{\eta\zeta}(r) \sim q_{\eta}q_{\zeta}/r. \quad (\text{I.82})$$

If the molecular species under consideration is electrically neutral, the sum of force-center charges for each molecule of course must vanish:

$$\sum_{\eta} q_{\eta} = 0. \quad (\text{I.83})$$

Formally, the dipole moment magnitude due to force-center charges for a molecule is

$$\mu = \left| \sum_{\eta} q_{\eta} \mathbf{u}_{\eta} \right|. \quad (\text{I.84})$$

In creating an appropriate $v_{\text{eff}}^{(2)}$ for a strongly polar molecule, this dipole magnitude may differ from that of the isolated molecule. In the case of water, the value required for optimal condensed-phase modeling may be substantially larger than that of the isolated species because of mutual polarization effects between each molecule and those comprising its surroundings. Various forms

of evidence suggest that μ should increase from the dilute gas value 1.855 D [Dyke and Muentzer, 1973] to approximately 2.95 ± 0.20 D in the liquid-water phase [Gubskaya and Kusalik, 2002]. Similar enhancements should be expected for other polar molecules embedded in condensed phases.

If stable ionic species such as the ammonium cation (NH_4^+) or sulfate anion (SO_4^{2-}) are present, the sums $\sum q_\eta$ for all such species should be integer multiples of a “unit charge.” However, the optimal choice for the force-center functions $b_{\eta\zeta}(r)$ may not set this “unit charge” equal to the fundamental proton charge e because of the need to account for dielectric polarization effects.

A comparative discussion of effective pair potentials for water, consisting of rigid molecules with simple force centers, may be found in Jorgensen et al. (1983). An example of force-center assignment for the normal-alkane homologous series appears in a publication by Errington and Panagiotopoulos (1999). Other chemical substances for which simple force-center approximations to intermolecular interactions have been proposed are the linear carbon disulfide molecule (CS_2) [Ciccotti et al., 1982], acetone (CH_3COCH_3) and chloroform (CHCl_3) [Rickardi et al., 1998], and various aromatic hydrocarbons [Williams, 1966].

The force-center functions devised for effective pair potentials can also be useful for modeling some aspects of intramolecular interactions comprised in $v^{(1)}$. This method becomes especially relevant when high-molecular-weight species such as long-chain alkanes, nonbiological polymers, or proteins are under consideration. Physically attainable conformations for those species can bring remote portions of the same molecule with their assigned force centers into close contact, in which case the resulting local contribution to the potential energy would be substantially indistinguishable from a corresponding intermolecular contribution that involves the same kind of local groupings of atoms.