

(20) The free-electron model is the simplest picture of electronic structure for extended solids, but it is clearly inappropriate for non-conducting solids and even does a relatively poor job for most metals. Nevertheless, the free-electron model introduces important concepts for the electronic structure of solids and is a reasonable starting point for *normal metals*, like sodium, magnesium, and aluminum. There are two fundamental assumptions in the free-electron model:

- The positive ions are *smearred out*, so the electrons are not affected by a lattice. This picture motivates the synonymous term *jellium* for this model.
- The electrons move *independently* of one another, i.e., each electron feels the average repulsive field from all other electrons.

These two interactions, the attraction between the free-electron *gas* and the uniform positive background and the average repulsion within the free-electron gas, exactly cancel each other, which makes the total potential energy for electrons equal to zero. The critical parameter of this model is the *number density of free electrons* $\rho(\mathbf{r}) \equiv \rho$, which is constant throughout the volume V of the solid. If this volume contains N free (valence) electrons, then the number density $\rho = N/V$ is uniform throughout the volume of the solid from which another synonym arises: the *homogeneous electron gas*.

The Schrödinger equation for free electrons is just the kinetic energy:

$$-\frac{\hbar^2}{2m}\nabla^2\psi_{\mathbf{k}}(\mathbf{r}) = E_{\mathbf{k}}\psi_{\mathbf{k}}(\mathbf{r}).$$

For a cubic volume with side L , the solutions to this equation use periodic boundary conditions $\psi_{\mathbf{k}}(x+L, y, z) = \psi_{\mathbf{k}}(x, y, z)$, $\psi_{\mathbf{k}}(x, y+L, z) = \psi_{\mathbf{k}}(x, y, z)$, and $\psi_{\mathbf{k}}(x, y, z+L) = \psi_{\mathbf{k}}(x, y, z)$. For an electron described by this wavefunction, as it moves and reaches one wall of the cube, it re-emerges on the opposite side rather than continuing outside the box. These periodic boundary conditions are called the Born-von Karman boundary conditions and generate the *quantum numbers* or *wavevectors* \mathbf{k} for motion along each dimension of the box $\mathbf{k} = (k_x, k_y, k_z)$. The solutions of this problem are:

- The *wavefunctions* are plane waves $\psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{V}}e^{i\mathbf{k}\cdot\mathbf{r}} = \frac{1}{\sqrt{V}}e^{i(k_x x + k_y y + k_z z)}$. These functions are periodic along a line parallel to the direction of \mathbf{k} . The wavefunctions for different wavevectors $\psi_{\mathbf{k}}(\mathbf{r})$ and $\psi_{\mathbf{k}'}(\mathbf{r})$ are *orthogonal*:

$$\int \psi_{\mathbf{k}'}^*(\mathbf{r}) \psi_{\mathbf{k}}(\mathbf{r}) dV = \frac{1}{V} \int e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}} dV = \delta(\mathbf{k}-\mathbf{k}') \equiv \langle \mathbf{k}' | \mathbf{k} \rangle.$$

The last symbol in the equation is the *Dirac bra-ket notation* for the overlap integral between $\psi_{\mathbf{k}}(\mathbf{r})$ and $\psi_{\mathbf{k}'}(\mathbf{r})$. The *Dirac delta function* $\delta(\mathbf{x}) = 0$ if $\mathbf{x} \neq \mathbf{0}$, and $\delta(\mathbf{x}) \neq 0$ if $\mathbf{x} = \mathbf{0}$.

- The *wavevectors* $\mathbf{k} = (k_x, k_y, k_z) = \frac{2\pi}{L}(n_x, n_y, n_z)$ form a discrete, quantized set of points because $V = L^3$ is finite. Therefore, the coordinates n_x, n_y, n_z are positive, negative, or zero integers and forms a cubic array of \mathbf{k} -points. Since the distance between adjacent \mathbf{k} -points is $\frac{2\pi}{L}$, then each wavevector occupies a volume $\left(\frac{2\pi}{L}\right)^3 = \frac{8\pi^3}{V}$. The region of these wavevectors is called *reciprocal space* because the units of the wavevectors are “1/length” such as 1/cm. Also, since each wavevector represents an electronic state of the free-electron gas, then the density of states is the number of \mathbf{k} -points per volume or $\frac{V}{8\pi^3}$. Therefore, as the volume of free electron box increases, the density of states also increases, so that the wavevectors adopt a *quasi-continuous* set of values in reciprocal space.

- The *energy* for the state $\psi_{\mathbf{k}}(\mathbf{r})$ is $E_{\mathbf{k}} = \frac{\hbar^2}{2m} |\mathbf{k}|^2 = \frac{\hbar^2 k^2}{2m}$, and it is entirely kinetic energy. Therefore, $E_{\mathbf{k}} \geq 0$ and $\hbar \mathbf{k} = \mathbf{p}$, the electron momentum. As a result, the deBroglie wavelength for electrons in the state $\psi_{\mathbf{k}}(\mathbf{r})$ is $\lambda = \frac{h}{p} = \frac{2\pi}{k}$. Furthermore, electronic states with equal and opposite momenta, i.e., $\psi_{+\mathbf{k}}(\mathbf{r})$ and $\psi_{-\mathbf{k}}(\mathbf{r})$, are degenerate $E_{-\mathbf{k}} = E_{+\mathbf{k}}$.

(21) Band Structure: The energies $E_{\mathbf{k}}$ for the wavefunctions $\psi_{\mathbf{k}}(\mathbf{r})$ can be plotted in a graph $E_{\mathbf{k}}$ vs. k , which is a parabola centered at $k = 0$ when plotted for $+k$ and $-k$. Each wavefunction or state can accommodate up to 2 electrons. At $T = 0$ K, all states $\psi_{\mathbf{k}}(\mathbf{r})$ are occupied such that $k \leq k_F$, called the *Fermi wavevector*. The energy of $\psi_{k_F}(\mathbf{r})$ is called the Fermi level E_F :

$$E_F = \frac{\hbar^2 k_F^2}{2m}.$$

The region of occupied states in reciprocal space is a sphere with radius k_F ; the surface of this region is called the *Fermi surface*. The Fermi wavevector is significant in the free-electron model because it depends on the number of free electrons N :

$$N = 2 \left(\frac{\# \mathbf{k} \text{ points}}{\text{volume}} \right) (\text{volume of occupied } \mathbf{k} \text{ space}) = 2 \left(\frac{V}{8\pi^3} \right) \left(\frac{4\pi}{3} k_F^3 \right) = \frac{V k_F^3}{3\pi^2}.$$

Therefore, the number density ρ sets the position of the Fermi wavevector:

$$\frac{N}{V} = \frac{k_F^3}{3\pi^2} \quad \text{or} \quad k_F = \left(3\pi^2 \frac{N}{V} \right)^{1/3} = (3\pi^2 \rho)^{1/3}.$$

An alternative expression of the number density ρ is the radius r_s of the sphere containing one free electron. The volume of this sphere is the volume per electron: $V/N = 1/\rho$, so that

$$r_s = \left(\frac{3}{4\pi} \right)^{1/3} \frac{1}{\rho^{1/3}} = \frac{0.6204}{\rho^{1/3}}.$$

Units are critical. To simplify expressions, the fundamental unit of distance is the Bohr radius $a_0 = 0.529 \text{ \AA}$, also called an *atomic unit (au)*, and the fundamental unit of energy is the Rydberg $hcR_{\infty} = 13.6 \text{ eV}$. In terms of fundamental physical constants, these units are:

$$\begin{aligned} a_0 &= \frac{(4\pi\epsilon_0 c^2) \hbar^2}{m e^2 c^2} = \frac{(10^7)(1.0546 \times 10^{-34} \text{ J} \cdot \text{sec})^2}{(9.1096 \times 10^{-31} \text{ kg})(1.6022 \times 10^{-19} \text{ coul})^2 (2.9979 \times 10^8 \text{ m/s})^2} \\ &= 5.29 \times 10^{-11} \text{ m} = 0.529 \text{ \AA} \equiv 1 \text{ au.} \\ hcR_{\infty} &= \frac{m e^4 c^4}{2(4\pi\epsilon_0 c^2)^2 \hbar^2} = \frac{(9.1096 \times 10^{-31} \text{ kg})(1.6022 \times 10^{-19} \text{ coul})^4 (2.9979 \times 10^8 \text{ m/s})^4}{2(10^7)^2 (1.0546 \times 10^{-34} \text{ J} \cdot \text{sec})^2} \\ &= 2.18 \times 10^{-18} \text{ J} = 13.6 \text{ eV} \equiv 1 \text{ Ryd.} \end{aligned}$$

Chemists more frequently use the energy units kilojoules per mole or kilocalories per mole:

$$1 \frac{\text{eV}}{\text{atom}} = 96.53 \frac{\text{kJ}}{\text{mol}} = 22.96 \frac{\text{kcal}}{\text{mol}}.$$

In terms of the radius r_s (in au) of the sphere containing one free electron, then:

$$\begin{aligned} \text{Electron (number) density (in } 1/\text{au}^3\text{):} & \quad \rho = \frac{0.239}{r_s^3} \\ \text{Fermi energy (in Ryd):} & \quad E_F = \frac{3.68}{r_s^2} = 9.56 \rho^{2/3} \\ \text{Fermi wavevector (in } 1/\text{au):} & \quad k_F = \frac{1.92}{r_s} = 3.09 \rho^{1/3} \end{aligned}$$

This simple model for electrons in a solid is useful to describe properties of simple metals such as electrical conduction when an external potential is applied. Based on the band structure, the degeneracy of $E_{-\mathbf{k}}$ and $E_{+\mathbf{k}}$ is broken when an electric field is applied to the free-electron gas because states $\psi_{+\mathbf{k}}(\mathbf{r})$ are lowered in energy whereas states $\psi_{-\mathbf{k}}(\mathbf{r})$ are raised in energy. Since there is no energy gap at E_F , the number of electrons with momenta $+\hbar\mathbf{k}$ exceeds the number with momenta $-\hbar\mathbf{k}$ and there is net electronic transport (conduction).

(22) The electronic *density of states (DOS)* describes the distribution of electronic states vs. energy. The part of the electronic DOS occupied by electrons can be essentially observed from valence band spectra obtained by photoelectron spectroscopy, although the measured intensities include the cross sections for ejecting photoelectrons from the various elements in the sample. The density of states at energy E is defined as the number of states $dN(E)$ in a small energy window dE around E . This function for the free electron gas can be determined by considering the total number of electrons that occupy states below some energy value $E = E_{\mathbf{k}}$. Let $N(E) = \#$ states of both spins with energies $\leq E = E_{\mathbf{k}}$:

$$N(E) = \frac{Vk^3}{3\pi^2} = \left(\frac{V}{3\pi^2}\right) \left(\frac{2m}{\hbar^2}\right)^{3/2} E^{3/2} = V \left(\frac{\rho}{E_F^{3/2}}\right) E^{3/2}.$$

Then, the DOS $n(E)$ is the derivative of $N(E)$ with respect to E :

$$n(E) = \frac{dN(E)}{dE} = \left(\frac{V}{2\pi^2}\right) \left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2} = \frac{3}{2} V \left(\frac{\rho}{E_F^{3/2}}\right) E^{1/2},$$

which is typically plotted with $n(E)$ on the vertical axis and E along the horizontal axis.

The electronic DOS can be used to evaluate various integrated properties of the free electron gas such as the number of conduction (valence) electrons, the average kinetic energy per electron, and various temperature-dependent properties. These values are calculated by integrating a weighted expression of the DOS over all occupied states because the energy states $\psi_{\mathbf{k}}(\mathbf{r})$ form a quasi-continuous band $E_{\mathbf{k}}$. Therefore,

$$\begin{aligned} N &= \# \text{ conduction (valence) electrons} \\ &= \int_0^{E_F} n(E) dE \\ U_{KE} &= \text{Average kinetic energy of the free electron gas} \\ &= \int_0^{E_F} E n(E) dE = \frac{3}{5} E_F = \frac{2.21}{r_s^2} \text{ (in Ryd)} \end{aligned}$$

For temperature-dependent properties $Q(T)$, the Fermi-Dirac distribution $f_{\text{FD}}(E, T)$ must be included in the integration, because it describes the occupied states for temperature T :

$$Q(T) = \int_0^{\infty} Q(E) n(E) f_{\text{FD}}(E, T) dE \sim \int_0^{\infty} \frac{Q(E) n(E)}{e^{(E-\mu)/kT}} dE, \quad \mu = \text{Chemical Potential.}$$

These integrals are evaluated using the Sommerfeld expansion, which is useful when $kT \ll \mu$:

$$\int_{-\infty}^{\infty} \frac{F(E)}{e^{(E-\mu)/kT} + 1} dE \approx \int_{-\infty}^{\mu} F(E) dE + \frac{\pi^2}{6} (kT)^2 \left. \frac{dF}{dE} \right|_{E=\mu} + \mathcal{O}\left(\frac{kT}{\mu}\right)^4.$$

Since $k = 8.617 \times 10^{-5}$ eV/K and $\mu \sim$ few eVs, then temperatures less than 1000 K will satisfy the conditions when this expansion provides valid conclusions. Using the Sommerfeld expansion, the chemical potential is related to the Fermi level as:

$$\mu \approx E_F - \frac{\pi^2 (kT)^2}{12 E_F}.$$

Some useful integrated thermodynamic properties of the free-electron gas include:

- Internal (kinetic) energy density: $u \equiv \frac{U_{KE}}{V} \sim \frac{3}{5} \rho E_F + \frac{\pi^2 \rho}{4 E_F} (kT)^2$ (J/m³)
- Heat capacity at constant volume: $c_v = \left(\frac{\partial u}{\partial T}\right)_v \sim \frac{\pi^2 \rho}{2 E_F} k^2 T$ (J/K·m³)
 The heat capacity of the free-electron gas is linear with temperature.
- Entropy density: $s = \frac{S}{V} = \int \frac{c_v}{T} dT \sim \frac{\pi^2 \rho}{2 E_F} k^2 T$ (J/K·m³)
- Helmholtz free energy density: $f = \frac{F}{V} = u - Ts \sim \frac{3}{5} \rho E_F - \frac{\pi^2 \rho}{4 E_F} (kT)^2$ (J/m³)
- Pressure of free-electron gas: $P = -\left(\frac{\partial F}{\partial V}\right)_{\partial N, T} \sim \frac{2}{5} \rho E_F + \frac{\pi^2 \rho}{6 E_F} (kT)^2$ (Pa = N/m²)
- Enthalpy density: $h = \frac{H}{V} = u + P \sim \rho E_F + \frac{5\pi^2 \rho}{12 E_F} (kT)^2$ (J/m³)
- Gibbs free energy density: $g = \frac{G}{V} = h - Ts \sim \rho E_F - \frac{\pi^2 \rho}{12 E_F} (kT)^2$ (J/m³)

(23) How reliable is the free-electron model to describe the electronic structure of metals? Some fundamental properties of metals include cohesive energies (U_{coh}) and occupied valence bandwidths from valence band photoelectron spectra. Cohesive energy describes the energy needed to separate atoms in the solid to free gaseous atoms: $\mathbf{M}(s) \rightarrow \mathbf{M}(g)$. Now, there is *no bonding* in the free-electron model although the conduction (valence) electrons are kept within the solid by the smeared out positive background. Nevertheless, there is an optimal volume for the density of free electrons. For non-interacting electrons, the energy is entirely kinetic, which is positive valued. However, electrons do interact with each other via *exchange* and *correlation*: an electron in the free-electron gas repels *parallel spin* electrons by the Pauli exchange force and the Coulomb force, whereas it repels *antiparallel spin* electrons just by the Coulomb force. Thus, there is an exclusion hole around an electron of radius r_s which contains no electrons that can *screen* the surrounding positive charge. The size of this sphere is the effective volume of one electron. Therefore, the electron experiences an attractive exchange-correlation potential U_{XC} that varies as $1/r_s$.

Applying exchange to the free-electron Schrödinger equation by applying the Hartree-Fock approximation leads to the eigenvalues, i.e., energies,⁷

$$E_k = \frac{\hbar^2 k^2}{2m} - \frac{e^2 k_F}{\pi} \left(1 + \frac{k_F^2 - k^2}{2k_F k} \ln \left| \frac{k_F + k}{k_F - k} \right| \right).$$

Integrating the second term over the occupied states $\psi_k(\mathbf{r})$ for $k \leq k_F$ gives the average exchange energy per electron U_X as

$$U_X = -\frac{3 e^2 k_F}{4 \pi} = -\frac{3 e^2}{4 \pi} (3\pi^2 \rho)^{1/3} = -\frac{0.916}{r_s} \text{ (in Ryd)}.$$

Including correlation is much more difficult mathematical problem with exact analytical solutions available only in the limits of high density ($r_s \rightarrow 0$) and low density ($r_s \gg 1$). A useful expression for the exchange-correlation energy per electron U_{XC} for the free electron gas is

⁷ N. Ashcroft and H. Mermin, *Solid State Physics*,

$$U_{XC} \sim -\frac{0.916}{r_s} - (0.115 - 0.0313 \ln r_s) \text{ (in Ryd)}.$$

Therefore, the average binding energy per electron of the free-electron (*FE*) gas is the sum of the average kinetic energy (*KE*) and average exchange-correlation energy (*XC*):

$$U_{FE} = U_{KE} + U_{XC} = \frac{2.210}{r_s^2} - \frac{0.916}{r_s} - (0.115 - 0.0313 \ln r_s) \text{ (in Ryd)},$$

with r_s expressed in au. The repulsive kinetic energy and attractive exchange-correlation energy give a shallow minimum of $U_{FE} = -0.16 \text{ Ryd}/e^- = -2.18 \text{ eV}/e^-$ at $r_s = 4.23 \text{ au} = 2.23 \text{ \AA}$. The value of r_s is close to the value for sodium. The reference “state” for the average binding energy of the free-electron gas is an infinite radius for the sphere of one conduction electron. Therefore, $-U_{FE}$ should be a reasonable approximation to the cohesive energy of sodium, which is 1.11 eV. The magnitudes of the average binding energies per electron are typically smaller than cohesive energies for the alkali and alkaline earth metals, which indicates that including the positive cores are important to establish reasonable models of electronic structure to replicate cohesive energies. The following table lists results for a few simple metals:

Element	Z	r_s (Å)	$-U_{FE}$ (eV)	U_{coh}/Z (eV)	E_F (eV)	Occupied Bandwidth
Li	1	1.72	2.05	1.63	4.76	~4.0
Na	1	2.08	2.21	1.11	3.26	~3.2
K	1	2.57	2.18	0.93	2.18	~2.6
Be	2	0.99	-0.63	1.66	14.28	~12.9
Mg	2	1.41	1.59	0.76	7.07	~6.9
Ca	2	1.73	2.06	0.92	4.62	~3.3

Another experimental feature of the electronic structure is the energy bandwidth of occupied electronic states. This can be estimated from the Fermi level because the occupied free energy band E_k is a parabola for $0 \leq k \leq k_F$, i.e., for energies $0 \leq E_k \leq E_F$. These values are included in the table and show very reasonable agreement with experiment. Therefore, the free electron model is useful for introducing important concepts and terms describing the electronic structure of solids. However, the amount of chemical information it provides is limited.

(24) The *DOS curves for various main group metallic elements* deviate significantly from the free-electron DOS curve, which varies as \sqrt{E} . The elements best described by this model are the 3rd period metals Na, Mg, and Al, but even their DOS curves exhibit perturbations (oscillations) around the corresponding Fermi levels. The 2nd and 3rd period elements have just *s* and *p* valence atomic orbitals. However, the DOS curves for Li and Be differ significantly from those of Na and Mg. Above ~1 electron/atom, the DOS curves for Li and Be drop, whereas those for Na and Mg do not. For the 4th, 5th, and 6th period alkali and alkaline earth metals, the DOS curves reveal the importance of virtual *d* orbitals. For metals Ga, In, and Tl, each DOS curve has its own distinctive features: for Ga, which adopts a complex orthorhombic structure consisting of condensed Ga–Ga dimers, there are many peaks and valleys in the DOS with the Fermi level falling in a deep minimum; for In, which is face-centered tetragonal, the DOS is nearly free electron-like; for Tl, the 6*s* states separates from the 6*p* states, an outcome that arises from relativistic effects. Lastly,

the DOS curves of the Group 11 and 12 metals Cu, Ag, Au and Zn, Cd, Hg include valence d bands below the corresponding Fermi levels. For Cu, Ag, Au, these d bands are much broader than they are for Zn, Cd, and Hg, which arises from the differences in effective nuclear charges.

Differences in the DOS curves for metallic elements from the free-electron model arise by interactions between the core and valence electrons and the presence of low-lying virtual atomic orbitals that can overlap in the solid and contribute to the occupied DOS. Wavefunctions occupied by valence electrons must be *orthogonal* to both core electron orbitals and virtual orbitals. Moreover, there are no core "1p" orbitals in Li and Be, while K, Ca, Rb, Sr, Cs, and Ba have low-lying, virtual d orbitals that are unoccupied in the ground state gaseous atoms but contribute to the DOS below the corresponding Fermi levels and influence the features of these curves. Overall, the best agreement occurs for Na, Mg, Al, which exhibit *nearly-free-electron* behavior.

Improvements to the free-electron model involve: (a) introducing a *periodic potential* to represent the electron-nuclear attraction from a periodic array of atoms; and (b) modifying the potential appropriately to represent the orthogonal relationship between wavefunctions for the valence (conduction) electrons and the core electrons. In the *nearly-free-electron* model, the lattice of atoms creates a periodic potential that is treated as a perturbation of the electronic kinetic energy with wavefunctions $\psi_{\mathbf{k}}(\mathbf{r})$.

Interlude: Periodic Functions on a Bravais Lattice: The lattice concept is important for applications to diffraction and electronic structure of crystalline solids. The electron density of a crystal is a periodic function of the Bravais lattice: $\rho(\mathbf{r} + \mathbf{T}_{mnp}) = \rho(\mathbf{r})$, in which $\mathbf{T}_{mnp} = m\mathbf{a} + n\mathbf{b} + p\mathbf{c}$ ($m, n, p =$ integers) is a lattice vector. Therefore, the electron density has the total symmetry of the Bravais lattice. A periodic function is a plane wave $Ae^{i\varphi} = A \cos \varphi + iA \sin \varphi$. Then, the electron density can be expressed as $\rho(\mathbf{r}) = A(\mathbf{r})e^{i\varphi(\mathbf{r})}$ so that $A(\mathbf{r})$ also has the total symmetry of the Bravais lattice. Now, $\rho(\mathbf{r})$ is single valued for every \mathbf{r} , which implies that $\varphi(\mathbf{r}) = \mathbf{K} \cdot \mathbf{r}$ and \mathbf{K} has units 1/distance. Then,

$$\rho(\mathbf{r} + \mathbf{T}_{mnp}) = A(\mathbf{r} + \mathbf{T}_{mnp})e^{i\mathbf{K} \cdot (\mathbf{r} + \mathbf{T}_{mnp})} = A(\mathbf{r})e^{i\mathbf{K} \cdot \mathbf{r}} e^{i\mathbf{K} \cdot \mathbf{T}_{mnp}} = \rho(\mathbf{r})e^{i\mathbf{K} \cdot \mathbf{T}_{mnp}} = \rho(\mathbf{r}).$$

Therefore, $\mathbf{K} \cdot \mathbf{T}_{mnp} = 2\pi N$ for any integer N . As a result, the possible vectors \mathbf{K} form the set of *reciprocal lattice vectors* $\mathbf{K}_{hkl} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$ ($h, k, l =$ integers). The orientations of $\mathbf{a}^*, \mathbf{b}^*, \mathbf{c}^*$ relative to $\mathbf{a}, \mathbf{b}, \mathbf{c}$ means that

$$\mathbf{K} \cdot \mathbf{T}_{mnp} = 2\pi(hm + kn + lp).$$

Now, because there are many reciprocal vectors \mathbf{K}_{hkl} that satisfy the periodic condition above, the most general way to express the periodic function $\rho(\mathbf{r})$ is as a summation, called a *Fourier series*, over all possible reciprocal lattice vectors \mathbf{K}_{hkl} :

$$\rho(\mathbf{r}) = \sum_{h,k,l} Q_{hkl} e^{2\pi i(hm+kn+lp)}; \quad Q_{hkl} = Q(\mathbf{K}_{hkl}).$$

As shown, the *Fourier coefficients* Q_{hkl} in the summation provide the weighting factors for the plane waves in the expansion to give the overall function. These Fourier coefficients are the *structure factors* from an X-ray diffraction experiment, and they will be important in the nearly free electron model.

(25) The *nearly-free-electron model* builds off the free-electron model by changing the uniform positive background to a lattice of positive point charges that represents the positions of atoms and creates a weak periodic potential energy function $V(\mathbf{r})$ for the conduction (*nearly-free*) electrons. $V(\mathbf{r})$ can be expressed as a Fourier series:

$$V(\mathbf{r}) = V(\mathbf{r} + \mathbf{T}_{mnp}) = \sum_{h,k,l} V_{hkl} e^{i\mathbf{K}_{hkl} \cdot \mathbf{r}} = \sum_{h,k,l} V_{hkl} e^{2\pi i(hx+ky+lz)}.$$

\mathbf{K}_{hkl} are reciprocal lattice vectors determined from the real space lattice and $V_{hkl} = V(\mathbf{K}_{hkl})$ are the amplitudes (Fourier coefficients) for each plane wave $\exp(i\mathbf{K}_{hkl} \cdot \mathbf{r})$; the V_{hkl} values have units of energy and can be positive, negative, or zero, depending on the arrangement of the point charges. This periodic potential is treated as a perturbation on the free-electron model, so that we start with the wavefunctions of the free-electron model and then examine the effect of the periodic potential on these functions.

The Hamiltonian operator has the total symmetry of the lattice and the wavefunctions are linear combinations of specific plane waves:

$$\psi_{\mathbf{k}}^{(NFE)}(\mathbf{r}) = \sum_{h,k,l} c_{\mathbf{k}-\mathbf{K}_{hkl}} e^{i(\mathbf{k}-\mathbf{K}_{hkl}) \cdot \mathbf{r}} = \sum_{h,k,l} c_{\mathbf{k}-\mathbf{K}_{hkl}} \psi_{\mathbf{k}-\mathbf{K}_{hkl}}^{(FE)}$$

Since the potential is treated as a perturbation, then, if $E_{\mathbf{k}}^{(FE)} \approx E_{\mathbf{k}-\mathbf{K}_{hkl}}^{(FE)}$, i.e., $\mathbf{k} - \mathbf{K}_{hkl} \approx \pm \mathbf{k}$, the energies and wavefunctions are:

$$E_{\mathbf{k}}^{(NFE)} = \frac{\hbar^2 k^2}{2m} + V_{000} + \sum_{h,k,l} \frac{|V_{hkl}|^2}{E_{\mathbf{k}}^{(FE)} - E_{\mathbf{k}-\mathbf{K}_{hkl}}^{(FE)}} \approx \frac{\hbar^2 k^2}{2m} + V_{000},$$

$$\psi_{\mathbf{k}}^{(NFE)}(\mathbf{r}) \sim e^{i\mathbf{k} \cdot \mathbf{r}} + \sum_{h,k,l} \frac{V_{hkl}}{E_{\mathbf{k}}^{(FE)} - E_{\mathbf{k}-\mathbf{K}_{hkl}}^{(FE)}} e^{i(\mathbf{k}-\mathbf{K}_{hkl}) \cdot \mathbf{r}} \approx e^{i\mathbf{k} \cdot \mathbf{r}}.$$

The terms in the summations are ignored because the periodic potential is weak so that the Fourier coefficients of the potential energy are negligible compared to the free-electron energy difference in the denominator. Furthermore, the outcome reveals that the energies are periodic in reciprocal space. These bands are parabolic around every reciprocal lattice vector \mathbf{K}_{hkl} and displaced by the 0th-order Fourier coefficient of the potential energy:

$$E_{\mathbf{k}-\mathbf{K}_{hkl}}^{(NFE)} = \frac{\hbar^2 |\mathbf{k} - \mathbf{K}_{hkl}|^2}{2m} + V_{000}.$$

In 1-d, the lattice is a chain of points separated by distance a . The corresponding reciprocal lattice is the set of points $K_h = (2\pi/a)h$ and the nearly-free-electron energies are:

$$E_{k-K_h}^{(NFE)} = \frac{\hbar^2 (k - K_h)^2}{2m} + V_0.$$

The resulting *band structure*, i.e., energies plotted as a function of wavevector, is a series of parabolas centered at the “wavevectors” K_h and with minimum energy values V_0 . Because the energies are periodic in reciprocal space, all energy-related information is located within a region of reciprocal space of length $2\pi/a$. This region is selected to surround the reciprocal lattice point $K_0 = 0$, corresponding to $-\pi/a \leq k \leq \pi/a$. This region is called the (first) *Brillouin zone*. We return to the implications of the Brillouin zone when we address the tight-binding model.

(26) The expansion of the energies and wavefunctions for the nearly free electron model is allowed if and only if $\psi_{\mathbf{k}}^{(FE)}$ and $\psi_{\mathbf{k}-\mathbf{K}_{hkl}}^{(FE)}$ are *nondegenerate* wavefunctions. However, because $E_{\mathbf{k}}^{(FE)} = E_{-\mathbf{k}}^{(FE)}$, then degeneracies occur for wavevectors $\mathbf{k} = \mathbf{K}_{hkl}/2$, which are boundary points of the Brillouin zone. This is visible for the 1-d example: the parabola centered at $K_0 = 0$ rises until it reaches the boundary points $k = \pi/a$ and $-\pi/a$, at which it turns (or folds) back into the Brillouin zone, continuing to rise in energy. In other words, two energy parabolas intersect and create *degenerate* wavefunctions at the Brillouin zone boundaries.

The periodic potential energy allows plane waves with wavevectors that differ by a reciprocal lattice vector to interact with each other:

$$\langle \mathbf{k}' | V(\mathbf{r}) | \mathbf{k} \rangle = \sum_{h,k,l} V_{hkl} \langle \mathbf{k}' | \mathbf{k} + \mathbf{K}_{hkl} \rangle = V_{hkl} \delta(\mathbf{k} + \mathbf{K}_{hkl} - \mathbf{k}').$$

Therefore, the two wavefunctions $\psi_{\mathbf{K}_{hkl}/2}^{(FE)}$ and $\psi_{-\mathbf{K}_{hkl}/2}^{(FE)}$ can interact with each other and are not eigenfunctions of the nearly free electron Hamiltonian. With respect to wavevectors in the first Brillouin zone, only wavevectors on the boundary can interact with each other. For the 1-d problem, the plane waves $\psi_{\pi/a}(x) \sim e^{i\pi x/a}$ and $\psi_{-\pi/a}(x) \sim e^{-i\pi x/a}$ interact via the potential energy operator:

$$\langle \pi/a | V(x) | -\pi/a \rangle = V_h \delta(-\pi/a + K_h - (\pi/a)) = V_h \delta(K_h - 2\pi/a) = V_1.$$

This interaction term breaks the degeneracy of the free-electron wavefunctions, opening an energy gap at the Brillouin zone boundary and causing the two wavefunctions to mix with each other.

(27) To obtain the energies and wavefunctions at the Brillouin zone boundary, a 2×2 Hamiltonian matrix must be set up using $\psi_{\pi/a}(x)$ and $\psi_{-\pi/a}(x)$ as the basis:

$$H = \begin{pmatrix} \langle \pi/a | H | \pi/a \rangle & \langle \pi/a | H | -\pi/a \rangle \\ \langle -\pi/a | H | \pi/a \rangle & \langle -\pi/a | H | -\pi/a \rangle \end{pmatrix} = \begin{pmatrix} \frac{\hbar^2}{8ma^2} + V_0 & V_1 \\ V_1 & \frac{\hbar^2}{8ma^2} + V_0 \end{pmatrix}.$$

The diagonal Hamiltonian matrix elements are the free-electron energies displaced by the 0th-order Fourier coefficient of the periodic potential. The off-diagonal elements indicate the interaction term between the two basis wavefunctions. Solving Schrödinger's equation for this 2×2 Hamiltonian means solving the secular determinant, which yields the solutions:

$$\begin{aligned} E_{\pi/a}^{(-)} &= \frac{\hbar^2}{8ma^2} + V_0 - |V_1|; & \psi_{\pi/a}^{(-)} &\sim e^{i\pi x/a} - (\text{sign } V_1) e^{-i\pi x/a} \\ E_{\pi/a}^{(+)} &= \frac{\hbar^2}{8ma^2} + V_0 + |V_1|; & \psi_{\pi/a}^{(+)} &\sim e^{i\pi x/a} + (\text{sign } V_1) e^{-i\pi x/a} \end{aligned}$$

Therefore, the periodic potential opens an energy gap $2|V_1|$ at the Brillouin zone boundary and the features of the two wavefunctions depend on the sign of the Fourier coefficient V_1 . $\psi_{\pi/a}^{(-)}$ is the wavefunction at the bottom of the gap; $\psi_{\pi/a}^{(+)}$ is the wavefunction at the top of the gap.

(28) The Fourier coefficients V_{hkl} depend on the nature of the atomic potentials and represent how a nucleus and its core electrons interact with the conduction (valence) electrons of the metal. Negative coefficients imply an attractive nuclear potential for the valence electrons and their wavefunctions. On the other hand, positive coefficients imply a nuclear potential that is screened by core electrons. As the solutions to the 1-d problem indicate, there are two possible outcomes:

$$\begin{aligned} \text{If } V_1 < 0: & \quad \psi_{\pi/a}^{(-)} \sim e^{i\pi x/a} + e^{-i\pi x/a} = \cos(\pi x/a) \text{ has nodes between atomic nuclei;} \\ & \quad \psi_{\pi/a}^{(+)} \sim e^{i\pi x/a} - e^{-i\pi x/a} = \sin(\pi x/a) \text{ has nodes at atomic nuclei.} \end{aligned}$$

The lower energy wavefunction has electron density building up on atomic sites and is antibonding between atoms because of the node locations. The higher energy wavefunction has electron density between atomic sites, is bonding between atoms, and nodes intersect atomic sites, like p AOs.

$$\begin{aligned} \text{If } V_1 > 0: & \quad \psi_{\pi/a}^{(-)} \sim e^{i\pi x/a} - e^{-i\pi x/a} = \sin(\pi x/a) \text{ has nodes at atomic nuclei;} \\ & \quad \psi_{\pi/a}^{(+)} \sim e^{i\pi x/a} + e^{-i\pi x/a} = \cos(\pi x/a) \text{ has nodes between atomic nuclei.} \end{aligned}$$

The lower energy wavefunction has electron density between atomic sites, is bonding between atoms, and nodes intersect atomic sites, like p AOs. The higher energy wavefunction has electron density building up on atomic sites and is antibonding between atoms because of the node locations.

(29) Re-examination of the DOS curves of the elemental metals Li, Be, Na, and Mg reveals the effects of the periodic potential in different ways:

- For the 2nd period metals, there is a significant drop in the DOS just above the Fermi level for Li (1 valence electron) or at the Fermi level for Be (2 valence electrons). The band just below the energy gap in the band structure for the 1-d chain can hold up to 2 electrons. Therefore, we can infer negative Fourier coefficients V_{hkl} for these 2nd period metals.
- For the 3rd period metals, the DOS resembles the free-electron DOS with small oscillations near the Fermi level. Therefore, we conclude positive Fourier coefficients V_{hkl} for the 3rd period metals.

There are no energy gaps in any of the four DOS curves because the metals are 3-d structures. Although energy gaps open for wavevectors at the Brillouin zone boundaries, the 3-d Brillouin zones have many different faces along different directions in 3-d reciprocal space. Therefore, the DOS curves show oscillations but no clear energy gaps, like the model 1-d chain. Furthermore, the different qualitative features of the DOS curves for the 2nd and 3rd period metals originate from the valence and core orbitals of these elements. The valence orbitals for Li and Be are $2s$ and $2p$ and only $1s$ as a core orbital; the valence orbitals for Na and Mg are $3s$ and $3p$ with $1s$, $2s$, and $2p$ orbitals for the core. The lack of any core p orbitals of the 2nd period elements significantly affects their electronic structures and identifies an additional correction to the free-electron model.

(30) *Pseudopotentials*: The next improvement stage of the free-electron model recognizes that the conduction electrons are valence electrons, whereas every metal atom also has core electrons in orbitals that are localized at each atomic site. Therefore, the conduction electron wavefunctions must be orthogonal to the core electron wavefunctions. This *orthogonality*, which is due to the Pauli Exclusion Principle, creates a weak *pseudopotential* for the valence electrons. A simple example for an atom is an *empty-core* pseudopotential $v_{ps}(\mathbf{r})$, which is characterized by a core radius R_c . As the name implies, $v_{ps}(r) = 0$ for $0 \leq r \leq R_c$ and follows an attractive Coulomb potential $v_{ps}(r) = -Ze^2/r$ for $r > R_c$. In the metal, the periodic potential experienced by the valence (conduction) electrons is the sum of these atomic pseudopotentials over every atomic site. The Fourier coefficients for this pseudopotential V'_{hkl} are determined from the Fourier transform of the real space pseudopotential $v_{ps}(q)$:

$$v_{ps}(q) = \frac{1}{V} \int v_{ps}(r) e^{-iq \cdot r} d\mathbf{r} = -\frac{2E_F}{3} \frac{\cos qR_c}{1 + (q/\kappa)^2}, \quad \kappa = \frac{12\pi\rho}{E_F}.$$

Therefore, $v_{ps}(q) < 0$ for small q values and achieves its first zero value at $q = \pi/2R_c$, above which $v_{ps}(q) > 0$. This function oscillates with relatively small magnitudes such that $v_{ps}(q) \rightarrow 0$ as $q \rightarrow \infty$.

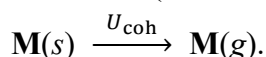
The Fourier coefficients of the periodic potential are $V'_{hkl} = v_{ps}(q = K_{hkl})$. By using the lattice constants for HCP Be ($a = 2.287 \text{ \AA}$, $c = 3.584 \text{ \AA}$) and Mg ($a = 3.209 \text{ \AA}$, $c = 5.211 \text{ \AA}$), the q values for the two shortest reciprocal lattice vectors K_{100} and K_{002} can be calculated and compared to $\pi/2R_c$:

$$\text{Be } (R_c = 0.402 \text{ \AA}): \quad K_{100} = 3.174 \text{ \AA}^{-1}, \quad K_{002} = 3.506 \text{ \AA}^{-1}, \quad \pi/2R_c = 3.907 \text{ \AA}^{-1};$$

$$\text{Mg} (R_c = 0.693 \text{ \AA}): \quad K_{100} = 2.261 \text{ \AA}^{-1}, \quad K_{002} = 2.412 \text{ \AA}^{-1}, \quad \pi/2R_c = 2.267 \text{ \AA}^{-1}.$$

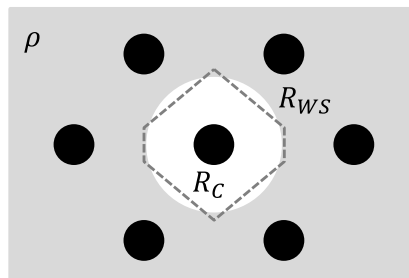
Since K_{100} and K_{002} for Be are less than 3.907 \AA^{-1} , the Fourier coefficients V'_{100} and V'_{002} are both less than 0. The smaller core radius indicates a more attractive potential for the conduction electrons near the Be cores. On the other hand, K_{100} and K_{002} for Mg are very close to and just above 2.267 \AA^{-1} , so that the Fourier coefficients V'_{100} and V'_{002} are nearly 0 or slightly positive. As a result, the potential slightly affects the band structure of Mg near Brillouin zone boundaries.

(31) Cohesive Energies of Simple Metals: The inclusion of a periodic pseudopotential to the free-electron gas provides a means to estimate the cohesive energy U_{coh} of a simple metal **M** with Z valence (conduction) electrons per atom:⁸



For this calculation, there are two important length scales:

- R_{WS} (Wigner-Seitz radius) = radius of the Wigner-Seitz sphere assigned to the Z valence electrons of the atom. The volume of the Wigner-Seitz sphere equals the volume of the Wigner-Seitz cell (dashed lines) surrounding each atom, i.e., it is the volume per atom in the unit cell of the structure.
- R_c (atomic core radius) = radius of the zero-potential sphere of the empty-core pseudopotential for the atom. Although R_c is an adjustable parameter, it is determined by minimizing the binding energy per atom, as discussed below.



The cohesive energy U_{coh} is calculated by breaking down the atomization process into three consecutive steps:

- (1) $\mathbf{M}(s) \xrightarrow{-ZU_{FE}} \mathbf{M}^{Z+}(s) + Ze^-(s)$: This step creates the nearly free electron gas of conduction electrons with the arrangement of nuclei plus their core electrons. The energy associated with the reverse of this step is the binding energy of the free-electron gas U_{FE} times the number of valence electrons Z :

$$\begin{aligned} ZU_{FE} &= \frac{2.210 Z}{r_s^2} - \frac{0.916 Z}{r_s} - (0.115 - 0.0313 \ln r_s) Z \quad (\text{in Ryd}) \\ &= \frac{2.210 Z^{5/3}}{R_{WS}^2} - \frac{0.916 Z^{4/3}}{R_{WS}} - (0.115 - 0.0313 \ln(Z^{-1/3} R_{WS})) Z \quad (\text{in Ryd}). \end{aligned}$$

In the second equation, the radius r_s associated with the sphere of one conduction electron is rescaled to the Wigner-Seitz radius by $R_{WS} = Z^{1/3} r_s$.

- (2) $\mathbf{M}^{Z+}(s) + Ze^-(s) \xrightarrow{-U_{ES}} \mathbf{M}^{Z+}(g) + Ze^-(g)$: The “second” step separates the valence electrons from the atomic cores. The energy of the reverse path is the *electrostatic energy* U_{ES} that holds the conduction electrons and atom cores together. Since each Wigner-Seitz cell is electrically neutral, this energy is approximated by considering just the attraction between the Z conduction electrons with the atomic core pseudopotential and the effective electron-electron repulsion within a single Wigner-Seitz sphere:

$$U_{ES} \approx -2 \int \rho v_{ps}(r) dr + 2 \int \frac{\rho \cdot \rho(r)}{r} dr = -\frac{3 Z^2}{R_{WS}} \left[1 - \left(\frac{R_c}{R_{WS}} \right)^2 \right] + \frac{1.2 Z^2}{R_{WS}} \quad (\text{in Ryd}).$$

⁸ L.A. Girifalco, *Acta Metallurgica*, **1976**, 24, 759-771.

A brief explanation of this equation is warranted: (i) interactions between Wigner-Seitz spheres are ignored because they are electrically neutral; (ii) the integral of the attractive potential between the constant electron density ρ and the atomic core is evaluated from R_c to R_{WS} ; (iii) the repulsive effective electron-electron repulsion is the electrostatic energy of a sphere of charge Z and radius R_{WS} ; and (iv) to use distances in atomic units and to obtain U_{ES} in Rydbergs, then $e^2 \equiv 2$.

The total binding energy of the conduction electrons is the minimum value of $ZU_{FE} + U_{ES}$. Since U_{ES} depends on R_{WS} and R_c , the minimum is obtained by evaluating R_{WS}^0 from the crystal structure of $\mathbf{M}(s)$ and then calculating R_c from:

$$\frac{d(ZU_{FE} + U_{ES})}{dR_{WS}} = 0: R_{WS} = R_{WS}^0 \quad \text{and} \quad \left(\frac{R_c}{R_{WS}^0}\right)^2 = \frac{1}{5} + \frac{0.102}{Z^{2/3}} + \frac{0.0035 R_{WS}^0}{Z} - \frac{0.491}{Z^{1/3} R_{WS}^0}.$$

- (3) $\mathbf{M}^{Z+}(g) + Ze^-(g) \xrightarrow{-I_Z} \mathbf{M}(g)$: The third step recombines the free valence electrons with the atomic core, which is the reverse of the ionization process. Therefore, the energy of the reverse process is the sum of the first Z ionization energies of the atom \mathbf{M} .

The cohesive energy of the simple metal $\mathbf{M}(s)$ with Z s and p valence electrons is calculated by the sum of the energies associated with these three hypothetical steps:

$$U_{coh}^{(calc)} = -ZU_{FE}(R_{WS}^0) - U_{ES}(R_{WS}^0; R_c) - I_Z.$$

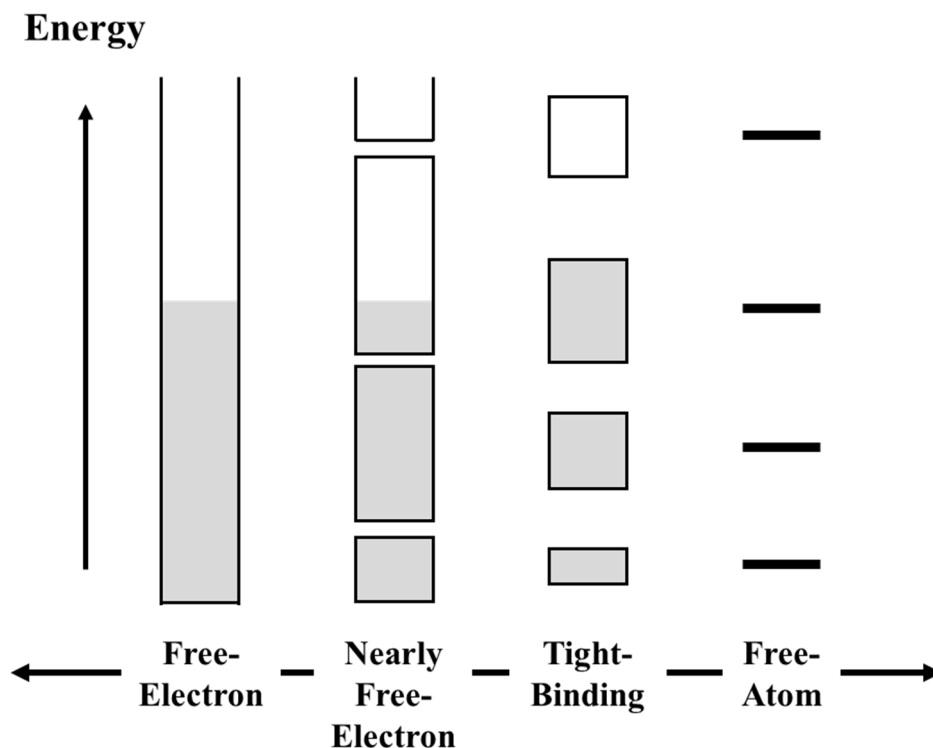
The following table summarizes the results of this calculation for various main group metals and compares the results with experimental values:

$\mathbf{M}(s)$	Z	R_{WS}^0 (Å)	R_c (Å)	$-ZU_{FE}$ (eV)	$-U_{ES}$ (eV)	I_Z (eV)	$U_{coh}^{(calc)}$ (eV)	$U_{coh}^{(exp)}$ (eV)
Li	1	1.728	0.698	2.057	5.458	5.392	2.123	1.643
Na	1	2.111	0.927	2.209	4.161	5.139	1.232	1.118
K	1	2.623	1.231	2.172	3.124	4.341	0.956	0.938
Cu	1	1.413	0.504	1.596	7.219	7.726	1.089	3.502
Be	2	1.246	0.400	-1.272	34.429	27.534	5.624	3.332
Mg	2	1.770	0.694	3.155	21.771	22.681	2.245	1.511
Ca	2	2.184	0.919	4.122	16.720	17.985	2.858	1.851
Zn	2	1.537	0.565	1.916	26.110	27.358	0.669	1.352
Al	3	1.582	0.589	0.816	56.632	53.263	4.186	3.402
Ga	3	1.673	0.637	1.976	52.836	57.223	-2.411	2.822

According to these results, most of the cohesive energy comes from the electrostatic energy term. However, this simple model neglects the specific crystal structure of the metal. Nonetheless, including an effect from the core electrons via an atomic core radius R_c provides reasonable estimates of U_{coh} for the third period elements Na, Mg, and Al, and trends in U_{coh} for the alkali and alkaline earth metals. On the other hand, estimates of U_{coh} for metals with $3d$ electrons as (pseudo)core electrons, i.e., Cu, Zn, and Ga are poor.

To summarize, electrons in the *free-electron* model move in an essentially constant potential so energies are kinetic with stabilization achieved by an exchange-correlation hole associated with each electron. The nearly-free-electron model includes a lattice of positive atomic cores that are

best described by a pseudopotential to consider the orthogonality between the wavefunctions of the core and conduction (valence) electrons. This pseudopotential is treated as a perturbation of the free-electron model, so that it is appropriate for main group metals like Na, Mg, Al, which have diffuse atomic orbitals and low ionization energies. Because the valence d orbitals for transition metals are more contracted and the d electrons are more tightly held by the atomic cores than the valence s and p electrons, the nearly-free-electron model is a poor starting point for the electronic structure of these elements. At the opposite end of the free-electron model is *tight-binding theory*, and the limit are the localized atomic orbitals of free atoms. In fact, using a fundamental Kronig-Penney model,⁹ one can illustrate an essential continuum in bonding models:



⁹ D. Pettifor, *Bonding and Structure of Molecules and Solids*, Clarendon Press, Oxford, 1995, pp. 112-116.