

(9) Quantum Mechanical Methods: Calculation of the electronic structure for a solid with N electrons involves solving the time-independent Schrödinger equation,

$$H\Psi_{\{n\}}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = E_{\{n\}}\Psi_{\{n\}}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N).$$

The Hamiltonian operator H contains all expressions to determine the kinetic and potential energies affecting the electrons, including possible external electric and magnetic fields. The electronic wavefunctions and their energies arise when appropriate boundary conditions are enacted. Also, since electronic motion involves speeds much larger than nuclear motions, the Born-Oppenheimer approximation, which fixes the nuclear positions in a structure, is applied. In the absence of any applied fields, then Hamiltonian for the N -electron system is:

$$H(\mathbf{r})\Psi_{\{n\}}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \sum_{i=1}^N \left(-\frac{\hbar^2}{2m} \nabla_i^2 - \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{j>i}^N \frac{1}{r_{ij}} \right) \Psi_{\{n\}}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N).$$

Electronic structure calculations are performed on static structures, even ignoring the zero-point motion of atoms at 0 K, so temperature is not a factor in such calculations. However, temperature affects how the spectrum of electronic states is occupied, which is described by a Fermi-Dirac distribution. Temperature can also affect the distribution of electronic states by any changes in atomic structure such as unit cell expansions or shrinkages. In the absence of such structural variations, temperature changes simply modify the occupation of electronic states. Nevertheless, when different atomic structures are considered as a function of temperature, then a Maxwell-Boltzmann distribution can be applied to evaluate a temperature-dependent Helmholtz free energy.

(10) Structure-Modelling Strategies: With respect to applying Schrödinger's equation to determine the electronic structure of a solid, every solid should be considered as *a molecule with a quasi-infinite number ($\sim 10^{23}$) of atoms*. Therefore, what strategies are available to tractably solve Schrödinger's equation for a solid-state structure? It helps to categorize solid-state structures into *molecular solids* or *extended structures*. For molecular solids, calculations are performed on the isolated molecule and often ignore the generally weaker but often more numerous intermolecular interactions, called *packing effects*. Sometimes these environmental factors can be treated as energetic perturbations on an individual molecule, or they can be modeled by some effective potential. Nevertheless, these weak intermolecular interactions can influence local molecular structures significantly, especially if these interactions are numerous. Among extended solids, there are three principal categories: (i) amorphous; (ii) aperiodic, which include modulated, intergrowths, and quasiperiodic; and (iii) crystalline, i.e., periodic. To treat the first two classes, fragments are often excised from the extended solid, such as silicate or phosphate oligomers from amorphous glasses or metal clusters from quasicrystals. So that no significant effects occur from abrupt surface termination at the fragments, they are terminated by simple atoms or local functions, such as pseudo-hydrogen atoms or s -type orbitals. The presence of translational symmetry in crystalline structures introduces an elegant simplification of the problem that allows very accurate calculations of bulk electronic states and properties. In fact, for aperiodic structures, calculations can be applied to crystalline *approximants*, which are periodic structures that resemble many of the local structural units of the aperiodic case. However, even for periodic structures, mixed site occupancies create challenges, which can be alleviated by using many different ordered model structures based on subgroups or super-structures, or by applying the coherent potential approximation.

(11) Potential Energy Terms: A major challenge for all electronic structure calculations is how best to treat the potential energy of the electrons. In the absence of any electron-electron

interactions, the Schrödinger equation can be solved exactly. The simplest approximation, called the *independent electron approximation*, uses the Hartree approximation in which each electron moves in the average electrostatic field $v_i(\mathbf{r}_i)$ of all other electrons. The multi-electron wavefunction Ψ is a product of one-electron wavefunctions ψ and the electron density is the sum of the individual electron densities at any given point \mathbf{r} :

$$\Psi_{\{n\}}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \psi_1(\mathbf{r}_1) \cdot \psi_2(\mathbf{r}_2) \cdots \psi_N(\mathbf{r}_N);$$

$$\rho(\mathbf{r}) = \sum_{i=1}^N |\psi_i(\mathbf{r})|^2.$$

This approach creates effective *single-particle* equations for each electron and the solutions are the one-electron wavefunctions, i.e., orbitals:

$$\left(-\frac{\hbar^2}{2m} \nabla_i^2 - \sum_{A=1}^M \frac{Z_A^{(\text{eff})}}{r_{iA}} + v_i(\mathbf{r}_i) \right) \psi_i(\mathbf{r}_i) = E_i \psi_i(\mathbf{r}_i).$$

Solving these equations require self-consistent calculations because the Hartree potential contains the electron density and the one-electron wavefunctions:

$$v_i(\mathbf{r}_i) = \int \frac{\rho(\mathbf{r}_j) - |\psi_i(\mathbf{r}_j)|^2}{|\mathbf{r}_i - \mathbf{r}_j|} d\mathbf{r}_j.$$

Thus, a good initial guess for these one-electron functions start the process and the Hartree potential is revised until some level of convergence is attained. However, the independent electron approximation is a drastic simplification.

So, the question remains, what is the best potential energy function to describe the electronic structure of a given solid? For simple metals, like Na, Mg, even Cu and Zn, the *free-electron*, *nearly-free-electron*, and *pseudopotential* methods provide increasingly better results; for transition metals, semimetals, semiconductors, and insulators, *pseudopotential* and *tight-binding* methods are generally preferred. Often, some type of hybrid approach is used to increase the accuracy of results while also providing means for sound physical and chemical interpretations.

(12) In general, the potential energy term of the Hamiltonian operator for an N -electron system can be divided into a *one-electron potential* and a *two-electron potential*. The effective one-electron potential includes the Hartree potential and the nucleus-electron attraction, in which the nuclear charge is replaced by an effective nuclear charge to account for screening of the valence electrons from the nucleus by any inner shells of electrons. Two-electron potentials include exchange ("X") and correlation ("C"). Exchange is a consequence of the indistinguishability of electrons and arises from electron spin. Spin- $1/2$ electrons follow Fermi-Dirac statistics so that when the information of two electrons are switched (*exchanged*) in a wavefunction, the wavefunction changes sign, for example $\Psi(\mathbf{r}_2, \mathbf{r}_1) = -\Psi(\mathbf{r}_1, \mathbf{r}_2)$. Correlation accounts for how each electron influences the behavior of every other electron through the repulsion of like charges. In fact, although exchange is conceptually difficult to understand, it can be readily calculated, whereas correlation is easier to understand but much more difficult to calculate accurately.

For the example of free electrons within a region, exchange and correlation create a *Fermi hole* around each electron. Consider a spin-up electron in a collection of free electrons with a homogeneous electron density ρ . If the interaction between spins is only considered, then down-spin electrons may approach the spin-up electron arbitrarily closely, but other spin-up electrons are repelled, according to the Pauli exclusion principle. If the charges of electrons are included,

then the combination of spin-based and charge-based repulsions create a hole in the electron density surrounding this spin-up electron. The overall positive charge inside this hole is +1, i.e., it has the same magnitude as the electronic charge. Together, the spin-up electron and the hole create a *quasi-particle* of radius r_s . Since this spherical region contains one electron, the radius r_s is inversely proportional to $\rho^{1/3}$. Now, free electrons are reasonable starting models for electrons in metals. Applying the Hartree-Fock method to the free electron wavefunctions by creating Slater determinants for the occupied wavefunctions to include exchange leads to a serious inconsistency. The resulting expression for the exchange energy of a one-electron function $E_X(\psi_i)$ yields infinite slope as E_i approaches the Fermi level E_F . As a result, when this exchange energy term is included, the electronic density of states goes to 0 at E_F , a result which contradicts the metallic behavior. Nevertheless, an average exchange energy per electron can be evaluated by averaging over all occupied states, which gives an expression that is inversely proportional to the one-electron Fermi hole radius r_s or, likewise, directly proportional to $\rho(\mathbf{r})^{1/3}$. This expression is a forerunner of the *local density approximation* (LDA) used in many electronic structure codes. Furthermore, expressions for the exchange potential include screening and some correlation effects. Therefore, this two-electron potential is generally expressed as a functional $v_{XC}\{\rho(\mathbf{r}_i)\}$.

(13) As mentioned above, exchange is more easily incorporated into the electronic Hamiltonian than is correlation. The local density approximation calculates the exchange energy term using a modification for the average exchange energy of a free electron gas with density ρ , which is replaced by the local charge density $\rho(\mathbf{r})$ throughout the solid-state structure. A more sophisticated estimation includes gradients of the charge density – the so-called *generalized gradient approximation* (GGA). In some cases, such as compounds containing rare earth metals with localized $4f$ electrons or certain $3d$ metal systems, correlation can be explicitly included by an *on-site e^-e^- repulsion* term U , leading to LDA+U for exchange and correlation. The simplest molecular orbital approach completely neglects any energy penalty for a single atomic orbital to be doubly occupied. As an example of this issue, consider an energetic comparison between two H atoms with the proton + hydride ion, i.e., $2 \text{H}(g)$ vs. $\text{H}^+(g) + \text{H}^-(g)$. The energy difference between these two extremes is $IE(\text{H}) - EA(\text{H}) = +12.9 \text{ eV}$, which would be an estimate of the on-site repulsion energy U for doubly occupying the H atom $1s$ atomic orbital. Therefore, weak correlation allows for a large degree of electronic delocalization and metallic behavior, whereas strong correlation tends toward electronic localization and insulating behavior. The transition between these types of metallic and insulating behaviors is called a Mott-Hubbard transition and the on-site repulsion term is called the Hubbard U parameter. To my knowledge, these U parameters are assigned values rather than calculated from first principles. Nevertheless, it is possible to vary the size of U to examine various outcomes.

(14) *Computational Approaches*: Results of electronic structure calculations are typically depicted in electronic *band structures* and *density of states* (DOS) curves, as illustrated for elemental silicon. Band structure diagrams are called “spaghetti curves” because of their resemblance to strings of pasta. Indeed, such a diagram is not reasonable for molecules. Nevertheless, the solid-state analogue of the molecular orbital energy diagram is the DOS curve. The goal of this unit is to become familiar with how these diagrams are obtained and identify what can be learned from this information.

(15) The general approach is to solve effective one-electron Schrödinger’s equation for the atomic arrangement of the solid. The eigenfunctions ψ_n of the Hamiltonian operator are expressed as

linear combinations of N basis functions φ_i , which can be atomic orbitals, plane waves, or some combination. The eigenvalues (energies) E_n of the Hamiltonian operator are the integrals

$$E_n = \int \psi_n^* H \psi_n d\mathbf{r} \equiv \langle \psi_n | H | \psi_n \rangle.$$

The definition specifies these integrals using the Dirac *bra-ket* notation. Now, with N basis functions, the Hamiltonian becomes an $N \times N$ matrix for which the secular determinant must be solved. In setting up the Hamiltonian matrix elements, there are *intra-site* (diagonal) integrals $\langle \varphi_i | H | \varphi_i \rangle$ and *inter-site* (off-diagonal) integrals $\langle \varphi_i | H | \varphi_j \rangle$. Lastly, it is important to recognize different energy scales: 1 Rydberg = 13.6 eV = 1313 kJ/mol = the ionization energy for the H atom. Also, 1 eV = 96.5 kJ/mol = 23.1 kcal/mol. Different scientific and disciplinary communities use different energy scales, depending on methods, values, etc. So, having these conversions in mind can help understand computational outcomes.

The Hamiltonian integrals include one-electron terms such as kinetic energy and electron-nuclear potential energy and two-electron terms such as coulombic repulsions and exchange-correlation interactions. Depending on how these integrals are determined identifies the general method type, which can range from mathematically simple to complex. *Empirical* or *semi-empirical methods* assign values to the integrals based on experimental data, such as AO energies for intra-site integrals, or by a simple algorithm, such as relating inter-site integrals to the spatial overlap of the interacting basis functions. Examples of these approaches include *Hückel* theory, *Extended Hückel* theory (EHT), and various *Neglect of Differential Overlap* (NDO) methods. In general, these relatively simple strategies utilize minimal basis sets, such as just valence atomic orbitals, which allow calculations to be completed rapidly. However, two-electron potential energy terms are explicitly ignored. Because of these simplifications, interatomic distances are poorly optimized and energy gaps for insulators and semiconductors are significantly overestimated. Nevertheless, these methods can be useful to examine trends either down a group or across a narrow stretch of a period of elements and the effects of symmetry are accurately represented. So, if structural symmetry is influential for the electronic structure, these simple methods can be very effective.

(16) *First-principles* methods mean that all integrals are explicitly calculated according to some physical model. These calculations typically give a more reliable determination of electronic states than empirical or semi-empirical methods, although their accuracy and appropriateness depend on the system and the models involved to express the electronic potential energy. The Hartree-Fock method is an *ab initio* method that incorporates anti-symmetrized wavefunctions via Slater determinants. Therefore, with exchange appropriately included, Hartree-Fock results are useful for insulators and semiconductors. However, in my opinion, this method is weaker for metals although it has been applied to metallic systems. A weakness of the Hartree-Fock theory is that it does not fully account for correlation because electrons move in a *mean field potential*. Therefore, the calculated eigenvalues tend to be too high, according to the variational theorem. To account for correlation, multiple Slater determinants are necessary, an improvement called *configuration interaction*.

(17) Density-functional theory (DFT) reformulates the solution to Schrödinger's equation using electron density. Developments of DFT, especially for treatment of the exchange-correlation potentials, make it the most accepted method for many types of problems. In general, DFT is very successful to predict or to replicate ground state properties of a chemical system, i.e., its atomic structure, charge density, bulk modulus, and any phase transitions that may occur under increased

pressure. However, energy gaps for semiconductors are usually underestimated because the method does not treat excited states (unoccupied orbitals) accurately. Nevertheless, exchange and correlation are explicitly treated via some physical approximation. Three common approaches are

- the *local density approximation* (LDA or GGA), which expresses the exchange-correlation potential using the local electron density or along with its gradients.
- the *local spin density approximation* (LSDA) decouples the two different electron spins by applying different potentials and using somewhat different basis functions.
- the *Hubbard-type correlation* LDA+U or LSDA+U, which includes on-site U parameters for certain elements, and is useful when there are strongly correlated electrons in the system. Examples where this level of calculation can be useful include rare-earth compounds with localized $4f$ electrons and transition metal oxides and halides with localized $3d$ electrons, such as in NiO(s).

(18) There are various codes available to carry out electronic structure calculations on solid-state structures. A comprehensive listing may be found at the Wikipedia page “List of quantum chemistry and solid-state physics software.” Some widely used software packages at this time (2024) include (listed in no particular order):

- VASP: <https://www.vasp.at/>
- Quantum Espresso: <https://www.quantum-espresso.org/>
- Wien2k: <http://susi.theochem.tuwien.ac.at/>
- Crystal: <https://www.crystal.unito.it/>

Regardless of the specific methods used by electronic structure codes, there are two fundamentally distinct philosophies that lead to models for solving Schrödinger’s equation in solids: (i) the *free electron* model; and (ii) the *tight-binding* model. In the free-electron model, the conduction electrons move in a constant potential with no lattice of atomic nuclei. This model is a reasonable starting point for most “simple” metals. The *nearly free electron* model introduces atomic nuclei, which can scatter electrons, and the next stage of improvement is *pseudopotentials*, which incorporates core-valence electron interactions. On the other hand, the tight-binding model begins with atoms, which hold their valence electrons tightly. This model closely resembles *molecular orbital theory* and utilizes linear combinations of basis functions that have been adapted to the symmetry of the solid. In tight-binding theory, the eigenfunctions can be analyzed or treated as “delocalized” Bloch functions or “localized” Wannier functions, depending on the types of questions and interpretations desired. An intermediate and somewhat hybrid philosophy is a *cellular approach*, which divides the structure into cells and can utilize both atomic-like and free-electron like potentials.

(19) In *cellular methods*, the solid is divided into Wigner-Seitz cells surrounding each atom. Since these cells are typically polyhedra, accurate calculation can be challenging and computationally demanding because the eigenfunctions must be continuous at the cell boundaries. One powerful approximation is to divide the potential energy space into two regions: non-overlapping spheres with radius R_{WS} around each atomic nucleus containing an atomic-like potential and the interstitial region between spheres containing a free-electron-like flat potential. Then, the eigenfunctions are atomic-like orbitals inside the spheres and plane waves outside the spheres. The boundary conditions are to match the two functions at the spherical boundaries. A further simplification eliminates the interstitial region by expanding the spherical regions so that their volumes equal the volumes of the corresponding Wigner-Seitz regions for each atom. As a

result, the spheres overlap, and this strategy is called the *atomic sphere approximation* (ASA). To increase computational speed further, the radial functions are linearized, which provides the foundation for the *linear muffin-tin orbital* (LMTO) approaches. Whereas these simplifications increase computational speed, an accurate description of the potential energy is sacrificed. There are also full-potential (FP) modifications available.