3 Tight-Binding Models and Coulomb Interactions for s, p, and d Electrons

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Contents

1   Introduction

The tight-binding method is the simplest fully quantum mechanical approach to the electronic structure of molecules and solids. Although less accurate than density functional calculations done with a good basis set, tight-binding calculations provide an appealingly direct and transparent picture of chemical bonding [1–10]. Easily interpreted quantities such as local densities of states and bond orders can be obtained from density-functional codes too, but emerge much more naturally in a tight-binding picture. Another advantage of tight-binding calculations is that they require much less computer time than more sophisticated electronic structure calculations, whilst still producing qualitatively and often quantitatively correct results. Chemists also value the efficiency and intuitive simplicity of the tight-binding method, although they usually refer to it as Hückel theory.

In non-interacting systems, tight-binding calculations are so simple that analytic results are often attainable — a rare occurrence in the study of electrons in molecules and solids. Interacting systems are much more difficult to deal with and the scope for analytic work is correspondingly smaller, but the multi-band Hubbard model, which may be viewed as an interacting generalization of a tight-binding model, forms the starting point of much of the work in the field.

Section 2 provides a simple introduction to tight-binding methods for non-interacting systems, showing how to obtain the Hamiltonian matrix by choosing a basis of localized atomic-like basis functions and using the variational principle. The distinction between the semi-empirical and ab-initio tight-binding methods is clarified and a few example semi-empirical tight-binding calculations are discussed.

Section 3 addresses the relationship between non-selfconsistent tight-binding models and density-functional theory, which was not fully understood until the late eighties [11, 12].

Section 4 introduces the multi-band Hubbard generalization of the tight-binding approximation and explains how it may be used to describe systems of interacting electrons. The rotational symmetry of the Coulomb interaction places strong restrictions on the form of the electron-electron interaction part of the multi-band Hubbard Hamiltonian: for an s shell the interaction Hamiltonian has only one free parameter; for a p shell there are two free parameters; and for a d shell there are three free parameters. It turns out that some of the most widely used Hubbard- and Stoner-like models of interacting electrons are missing terms that must be present by symmetry and are not necessarily small [13].

2   Tight-binding models

All electronic structure methods require the calculation of sets of one-electron orbitals $\psi_i(\boldsymbol{r})$. In most cases, these are solutions of a non-interacting or mean-field Schrödinger equation of the form[1]

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[1]This chapter uses dimensionless equations involving only the numerical values of physical quantities. The numerical values are as measured in Hartree atomic units, where the Dirac constant $\hbar = h/2\pi$, the mass of an electron m_e, and the elementary charge e are all equal to unity, and the permittivity of free space

$$\left(-\frac{1}{2}\nabla^2 + V_{\text{eff}}(\boldsymbol{r})\right)\psi_i(\boldsymbol{r}) = \epsilon_i\psi_i(\boldsymbol{r})\,. \tag{1}$$

The effective potential V_{eff} is a simple multiplicative function of position in density-functional theory (DFT), but in Hartree-Fock theory it becomes a non-local integral operator, and in quasi-particle theory it is both non-local and energy dependent.

Differential equations such as Eq. (1) are often solved by introducing a spatial grid and discretizing, but this approach is not much used in electronic structure theory. Instead, most electronic structure methods represent the orbitals as linear combinations of basis functions and recast the Schrödinger equation in matrix form. The finite-element approach so prevalent in engineering also uses a basis set, although the basis functions in that case are polynomials defined within polyhedral volume elements, patched together at the interfaces between elements. The clearest way to explain the basis-set approach is via the variational principle.

2.1 Variational formulation of the Schrödinger equation

The problem of finding the eigenfunctions of a Hamiltonian $\hat{H}$ is equivalent to the problem of finding the stationary points (by which, of course, I mean the stationary wave functions) of the functional

$$E[\psi] = \langle\psi|\hat{H}|\psi\rangle \tag{2}$$

subject to the normalization constraint

$$N[\psi] = \langle\psi|\psi\rangle = 1\,. \tag{3}$$

The constrained minimum value of $E[\psi]$ is the ground-state eigenvalue; the values of $E[\psi]$ at other stationary points are excited-state eigenvalues.

Suppose we make a guess, $\tilde{\psi}_i$, at the i'th energy eigenfunction ψ_i. We can then write

$$\tilde{\psi}_i = \frac{\psi_i + \Delta\psi_i}{\langle\psi_i + \Delta\psi_i|\psi_i + \Delta\psi_i\rangle^{1/2}},$$

where $\Delta\psi_i$ is small if the guess is good. Since $E[\psi]$ is stationary with respect to normalization-conserving variations about ψ_i, the energy estimate

$$E[\tilde{\psi}_i] = \epsilon_i + \mathcal{O}[(\Delta\psi_i)^2]$$

has a second-order error. If $\Delta\psi_i$ is small, the error in ϵ_i is even smaller.

The practical importance of this simple observation is hard to exaggerate. It explains why variational approaches often yield reliable energies even when the approximate eigenfunctions are quite poor.

ε_0 is equal to $1/(4\pi)$. Distances are made dimensionless by dividing by the Hartree atomic unit of length, $a_0 = 4\pi\varepsilon_0\hbar^2/(m_e e^2) \approx 0.529 \times 10^{-10}$ m, also known as the Bohr radius. Energies are made dimensionless by dividing by the Hartree atomic unit of energy, $\hbar^2/(ma_0^2) = e^2/(4\pi\varepsilon_0 a_0) \approx 27.2$ eV.

A convenient way to guess a wave function is to choose a finite set of M basis functions, $\{\phi_1(\boldsymbol{r}), \phi_2(\boldsymbol{r}), \ldots, \phi_M(\boldsymbol{r})\}$, and express $\tilde{\psi}(\boldsymbol{r})$ as a linear combination:

$$\tilde{\psi}(\boldsymbol{c}, \boldsymbol{r}) = \sum_{\alpha=1}^{M} c_\alpha \, \phi_\alpha(\boldsymbol{r}) \,. \tag{4}$$

Basis sets commonly used to approximate the energy eigenfunctions of atoms, molecules and solids include atom-centered Gaussians, plane waves, and atomic orbitals. The values of the expansion coefficients can be chosen by seeking the stationary points of

$$E[\tilde{\psi}] = E(\boldsymbol{c}) = \int \left(\sum_{\alpha=1}^{M} c_\alpha \phi_\alpha \right)^* \hat{H} \left(\sum_{\beta=1}^{M} c_\beta \phi_\beta \right) d^3r = \sum_{\alpha,\beta}^{M} c_\alpha^* \, H_{\alpha\beta} \, c_\beta \,, \tag{5}$$

subject to the normalization constraint

$$N[\tilde{\psi}] = N(\boldsymbol{c}) = \int \left(\sum_{\alpha=1}^{M} c_\alpha \phi_\alpha \right)^* \left(\sum_{\beta=1}^{M} c_\beta \phi_\beta \right) d^3r = \sum_{\alpha,\beta}^{M} c_\alpha^* \, S_{\alpha\beta} \, c_\beta = 1 \,, \tag{6}$$

where

$$H_{\alpha\beta} \equiv \int \phi_\alpha^* \hat{H} \phi_\beta = \text{Hamiltonian matrix,} \tag{7}$$

$$S_{\alpha\beta} \equiv \int \phi_\alpha^* \phi_\beta \quad = \text{overlap matrix.} \tag{8}$$

Given a basis set, the Hamiltonian and overlap matrix elements must be obtained by integration. The integrals can be evaluated analytically in some cases, but usually have to be estimated numerically, perhaps using a grid-based quadrature method. Some basis sets (such as plane waves) are orthonormal, in which case $S_{\alpha\beta} = \delta_{\alpha\beta}$ is the identity matrix. The Hamiltonian and overlap matrices are always Hermitian.

By choosing a finite basis set, we have replaced the problem of finding the stationary points of a functional $E[\tilde{\psi}]$ by the problem of finding the stationary points of a function of many variables $E(c_1, c_2, \ldots, c_M)$. This is a great simplification. If the basis set is poor, the functions $\tilde{\psi}(\boldsymbol{r}) = \sum_{\alpha=1}^{M} c_\alpha \, \phi_\alpha(\boldsymbol{r})$ that make $E(c_1, c_2, \ldots, c_M)$ stationary subject to the normalization constraint $\sum_{\alpha,\beta} c_\alpha^* S_{\alpha\beta} \, c_\beta = 1$ may not be very similar to the exact eigenfunctions, but at least we will have the variational principle in our favor when evaluating energies.

It is straightforward to show that $E(\boldsymbol{c})$ is stationary subject to $N(\boldsymbol{c}) = 1$ when

$$\sum_{\beta=1}^{M} H_{\alpha\beta} \, c_\beta = \tilde{\epsilon} \sum_{\beta=1}^{M} S_{\alpha\beta} \, c_\beta \,, \tag{9}$$

where $\tilde{\epsilon}$ is a Lagrange multiplier for the normalization constraint. This *generalized Hermitian matrix eigenproblem* ("generalized" because of the presence of a positive-definite Hermitian overlap matrix $\boldsymbol{S}$) yields M real eigenvalues $\tilde{\epsilon}_i$ and M eigenvectors $\boldsymbol{c}_i$ with components $c_{i\alpha}$, $\alpha = 1, 2, \ldots, M$. The corresponding approximate eigenfunctions are

$$\tilde{\psi}_i(\boldsymbol{r}) = \sum_{\alpha=1}^{M} c_{i\alpha} \phi_\alpha(\boldsymbol{r}) \,. \tag{10}$$

Standard computational libraries such as LAPACK contain robust and well-tested subroutines for solving generalized eigenvalue problems.

Another way to think about the linear variational method is in terms of projection operators. The generalized matrix eigenproblem of Eq. (9) may be derived by seeking the stationary points of $\langle\psi|\hat{P}\hat{H}\hat{P}|\psi\rangle$ subject to the normalization constraint $\langle\psi|\hat{P}|\psi\rangle = 1$, where $\hat{P}$ is the projector onto the space spanned by the basis functions. The linear variational method produces *exact* eigenfunctions of the *projected* Hamiltonian $\hat{H}^P \equiv \hat{P}\hat{H}\hat{P}$.

The Rayleigh-Ritz variational principle tells us that M approximate eigenvalues, $\tilde{\epsilon}_1$, $\tilde{\epsilon}_2$, ..., $\tilde{\epsilon}_M$, obtained by solving a linear variational problem with a basis set of M functions are upper bounds for the corresponding exact eigenvalues:

$$\tilde{\epsilon}_1 \geq \epsilon_1, \quad \tilde{\epsilon}_2 \geq \epsilon_2, \quad \ldots, \quad \tilde{\epsilon}_M \geq \epsilon_M.$$

Improving or extending the basis set can only lower these bounds. This convenient systematic convergence underlies the success of the linear variational approach and explains why it is so frequently used to solve the Schrödinger equation.

2.2   The tight-binding Hamiltonian matrix

If the basis functions used in the linear variational method are atomic or atomic-like orbitals, the generalized matrix eigenvalue problem is called a tight-binding model. The phrase "atomic-like" refers to orbitals that resemble atomic orbitals in form but have been modified in some way. Atomic orbitals centered on different atoms are not automatically orthogonal, so one common modification is to replace them by orthogonalized linear combinations. More generally, since there is no guarantee that atomic orbitals are a good basis for the strongly delocalized energy eigenfunctions found in many molecules and solids, one can often gain accuracy by changing the atomic orbitals in simple ways, using the variational principle as a guide. A more extreme approach is to replace the atomic orbitals by localized linear combinations of exact energy eigenfunctions for the solid, guaranteeing that the basis set is able to represent those eigenfunctions exactly.

2.2.1   *Ab initio* tight binding

The most straightforward way to construct a tight-binding model is to choose an atomic-like basis set and evaluate the Hamiltonian and overlap matrix elements defined in Eqs. (7) and (8). If the basis functions and (pseudo-)potential are represented as linear combinations of Gaussians, the necessary integrals can be evaluated analytically, but in most other cases they must be found using numerical quadrature methods. If one is willing to evaluate the matrix elements repeatedly as the charge density iterates to self-consistency and the effective potential changes (see Sec. 3 for a fuller discussion), this *ab initio* tight-binding approach [14–16, 7] can be used to solve the full DFT or Hartree-Fock equations.

When used in this manner, the tight-binding method differs little from the atom-centered Gaussian methods used by quantum chemists. There is, however, a difference of emphasis: scientists who label their approach as tight binding use minimal basis sets, often consisting of just a few

basis functions on each atom. They view the loss of accuracy caused by the limitations of the basis as a price worth paying for the sake of simplicity. Most quantum chemists prefer to increase the number of Gaussians until the results of their calculations converge.

Using a minimal basis set of atomic-like functions is most successful when the distances between atoms are reasonably large compared with the ranges of the basis functions. This is known as the tight-binding limit. In nearly-free-electron sp-bonded metals such as aluminium, where the valence wave functions look more like plane waves than atomic orbitals, minimal tight-binding basis sets are not very effective. This does not prevent the use of *ab initio* tight binding, but means that more basis functions are required to obtain accurate results. In d- and f-electron metals, the tight-binding description works better for the d and f bands than for the more delocalized s and p bands.

It is tempting to avoid the complication of dealing with an overlap matrix by orthogonalizing the basis functions. This is easily accomplished using the modified Gram-Schmidt algorithm or by multiplication with the inverse square root of the overlap matrix (which always exists because $\boldsymbol{S}$ is Hermitian and positive definite). In most cases, however, orthonormalizing the atomic-like basis functions is a bad idea. Generalized eigenvalue problems are not much harder to solve than ordinary eigenvalue problems, so little computer time is saved, but the complexity of the method is increased because the orthonormalized basis functions include contributions from atomic-like orbitals centered on several different atoms and lack the simple rotational symmetries of atomic-like orbitals. The complicated dependence of the orthonormalized orbitals on the local crystal structure also makes it harder to find simple parametrizations of the Hamiltonian matrix.

2.2.2   Wannier tight binding

A more sophisticated approach to *ab initio* tight binding is to use a basis of localized linear combinations of exact eigenfunctions; these are called Wannier functions by physicists and Foster-Boys orbitals by chemists [17,18]. Since there is one Wannier function for every energy eigenfunction, the Wannier functions span the band(s) from which they were created. Solving the tight-binding matrix eigenvalue problem in the Wannier function basis therefore reproduces those energy bands and eigenfunctions exactly. This means that using the Wannier basis for, say, electronic transport calculations, ought to give accurate results. The "maximally localized" [18] Wannier bonding orbitals for Si and GaAs are illustrated in Fig. 1.

Wannier-based tight-binding methods preserve many of the advantages of simpler tight-binding approaches without the inaccuracy, but Wannier functions are complicated in form and hard to calculate without solving the Schrödinger equation. Furthermore, although carefully constructed Wannier functions decay exponentially with distance away from the atom or bond on which they are centered [18], they may not decay rapidly. The Hamiltonian and overlap matrices can be quite long-ranged and may have non-zero matrix elements between Wannier functions on distant atoms, making them inconvenient to use. Finally, if an atom moves, the Wannier functions and all matrix elements involving them have to be recalculated from scratch, which is inefficient.
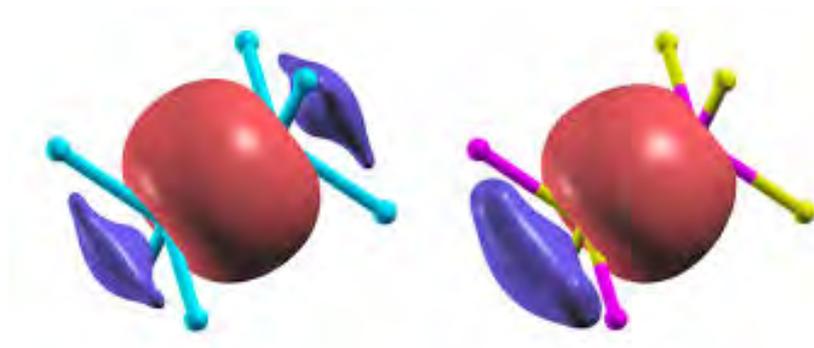
Fig. 1: *Maximally-localized Wannier functions constructed from the four valence bands of Si (left) and GaAs (right; Ga at upper right, As at lower left). The Wannier functions are real and have opposite sign on the blue and red isosurfaces. Not surprisingly, the functions look like σ-bonded combinations of sp^3 hybrid orbitals. (Reprinted figure with permission from Ref. [18], Copyright 2012 by the American Physical Society.)*

2.2.3   Semi-empirical tight binding

A much simpler approach is semi-empirical tight-binding [2, 3], in which the Hamiltonian and overlap matrix elements are treated as adjustable parameters and fitted to the results of experiments or more sophisticated calculations. The basis functions never appear explicitly and are used only to help justify the chosen forms of the Hamiltonian and overlap matrices. To limit the number of fitting parameters, it is normally assumed that the inter-atomic matrix elements extend to first or second neighbors only. Many semi-empirical tight-binding models also set the overlap matrix to the identity, assuming implicitly that the underlying basis set has been orthonormalized.

The drawbacks of this approach are obvious: it is approximate and may or may not give accurate results; but it does incorporate the essential wave-like physics described by the Schrödinger equation. To the best of my knowledge, it is the least computationally intensive fully quantum mechanical method available. To show what can be done using relatively modest computational resources, Fig. 2 is a snapshot from a 95 fs semi-empirical tight-binding molecular-dynamics simulation of a radiation damage cascade in a box of 13,440 Cu atoms subject to periodic boundary conditions.

2.2.4   One-, two- and three-center integrals

In an attempt to simplify the construction of semi-empirical tight-binding models, various approximations are made. The tight-binding description of the electronic structure of a given crystal structure then requires only a handful of fitting parameters. If the tight-binding model is to be used in a molecular-dynamics simulation, where the atoms are moving and the structure is changing, these parameters become functions of the local structure of the solid. For example, a Hamiltonian or overlap matrix element involving atomic-like basis functions on two different atoms is a function of the separation between those atoms and perhaps also of the positions of other neighboring atoms.
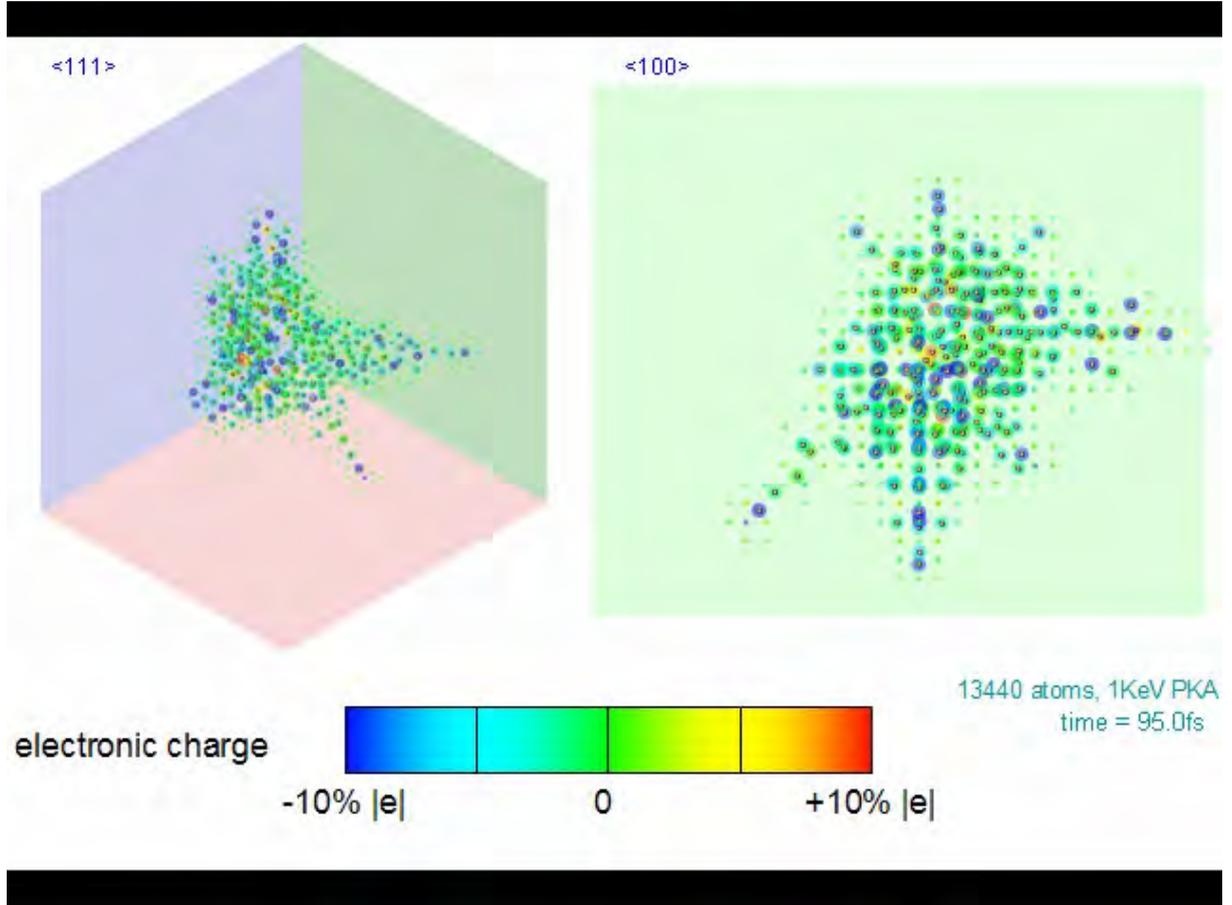
Fig. 2: *The final configuration of a 95 fs tight-binding molecular dynamics simulation of a radiation damage cascade in Cu. The cascade was initiated by giving 1 keV of kinetic energy to a single atom in the middle of a simulation cell of 13,440 atoms. Only atoms that have moved significantly are shown. One of the advantages of the tight-binding method relative to classical force-field methods is that it has access to electronic properties. Here we show the instantaneous atomic charges.*

The most useful approximation concerns the form of the potential $V_{\text{eff}}(\boldsymbol{r})$, which is often assumed to be a superposition of short-ranged spherical contributions, one centered on each atom:

$$V_{\text{eff}}(\boldsymbol{r}) \approx \sum_I V_{\text{eff},I}(|\boldsymbol{r} - \boldsymbol{d}_I|), \tag{11}$$

where $\boldsymbol{d}_I$ is the position of the nucleus of atom I (or the ionic core of atom I if, as is usual, the tight-binding model describes the valence electrons only). DFT calculations for many molecules and solids have shown that Eq. (11) is often quite a good approximation.

A general Hamiltonian matrix element between basis function α on atom I and basis function β on atom J then takes the form:

$$H_{I\alpha,J\beta} = \langle \phi_{I\alpha} | \hat{H} | \phi_{J\beta} \rangle = \langle \phi_{I\alpha} | \left(-\frac{1}{2} \nabla^2 + \sum_K V_{\text{eff},K}(|\boldsymbol{r} - \boldsymbol{d}_K|) \right) | \phi_{J\beta} \rangle. \tag{12}$$

If I and J happen to be the same, $I = J$, the matrix element includes one- and two-center

contributions:

$$\langle\phi_{I\alpha}|\hat{H}|\phi_{I\beta}\rangle = \underbrace{\langle\phi_{I\alpha}|\left(-\frac{1}{2}\nabla^2 + V_{\text{eff},I}\right)|\phi_{I\beta}\rangle}_{\text{one-center}} + \sum_{K\,(\neq I)}\underbrace{\langle\phi_{I\alpha}|V_{\text{eff},K}|\phi_{I\beta}\rangle}_{\text{two-center crystal field}}. \tag{13}$$

The one-center term can be calculated considering a single spherical atom in isolation. The two-center crystal-field terms, which are often ignored, depend on the relative positions of two different atoms and describe how the Hamiltonian matrix elements between orbitals centered on atom I are affected by the potential of atom K.

If I and J differ, the Hamiltonian matrix elements include two- and three-center contributions:

$$\langle\phi_{I\alpha}|\hat{H}|\phi_{J\beta}\rangle = \underbrace{\langle\phi_{I\alpha}|\left(-\frac{1}{2}\nabla^2 + V_{\text{eff},I} + V_{\text{eff},J}\right)|\phi_{J\beta}\rangle}_{\text{two-center electron hopping}} + \sum_{K\,(\neq I,J)}\underbrace{\langle\phi_{I\alpha}|V_{\text{eff},K}|\phi_{J\beta}\rangle}_{\text{three-center}}. \tag{14}$$

The two-center electron hopping contributions are the same as in a dimer involving atoms I and J only and can be calculated without considering the rest of the solid. The three-center contributions are typically small and, like the crystal-field terms, are often ignored. (Both crystal-field and three-center terms are normally retained in *ab initio* tight-binding calculations.) The overlap matrix elements can be decomposed in an analogous manner, but include one- and two-center contributions only.

If we make the two-center approximation (ignore all three-center integrals) and neglect crystal-field terms, the Hamiltonian matrix for a solid or molecule becomes very simple. It contains one-center terms, which can be calculated by considering an isolated "atom" with a spherical Hamiltonian, and two-center electron hopping terms, which can be calculated by considering an isolated "dimer" with a cylindrical Hamiltonian. The words "atom" and "dimer" are in quotation marks because the potential $V_{\text{eff},I}$ associated with atom I may not resemble the potential of an isolated atom and may depend on the environment in which atom I is located.

2.2.5 Slater-Koster parameters

Most tight-binding models use atomic-like basis functions of the form $R_{nl}(r)\tilde{Y}_l^m(\theta,\phi)$, where $R_{nl}(r)$ is a radial function, $\tilde{Y}_l^m(\theta,\phi)$ is a real spherical harmonic defined by

$$\tilde{Y}_l^m = \frac{1}{i\sqrt{2}}\left[(-1)^m Y_l^{-m} - Y_l^m\right], \qquad m < 0, \tag{15}$$

$$\tilde{Y}_l^m = Y_l^m, \qquad m = 0, \tag{16}$$

$$\tilde{Y}_l^m = \frac{1}{\sqrt{2}}\left[(-1)^m Y_l^m + Y_l^{-m}\right], \qquad m > 0, \tag{17}$$

and Y_l^m is a conventional complex spherical harmonic. The real spherical harmonics are the Cartesian s, p and d orbitals familiar from high-school chemistry lessons and are illustrated in Figs. 3 and 4.
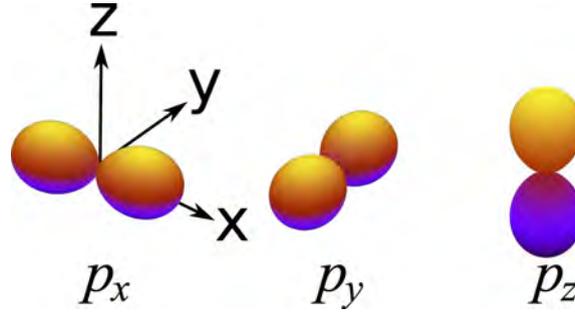
Fig. 3: *The real spherical harmonics $\tilde{Y}_1^1 = p_x$, $\tilde{Y}_1^{-1} = p_y$ and $\tilde{Y}_0^0 = p_z$. The distance from the origin to the surface in direction (θ,ϕ) is proportional to $|\tilde{Y}_l^m(\theta,\phi)|^2$*
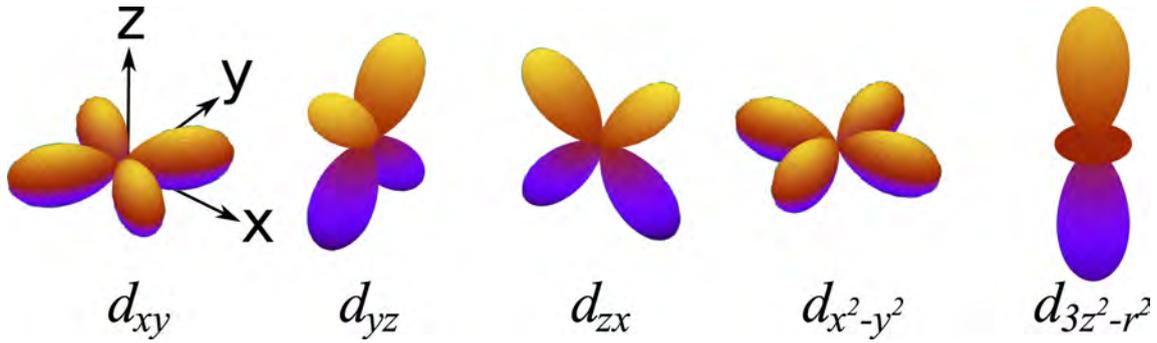
Fig. 4: *The $l = 2$ real spherical harmonics $\tilde{Y}_2^{-2} = d_{xy}$, $\tilde{Y}_2^{-1} = d_{yz}$, $\tilde{Y}_2^1 = d_{zx}$, $\tilde{Y}_2^2 = d_{x^2-y^2}$, and $\tilde{Y}_2^0 = d_{3z^2-r^2}$. The distance from the origin to the surface in direction (θ,ϕ) is proportional to $|\tilde{Y}_l^m(\theta,\phi)|^2$*

Because the effective potential $V_{\text{eff},I}$ of an atom is assumed to be spherically symmetric, there is only one non-zero one-center matrix element for every distinct choice of the compound index nl. Two-center matrix elements may be calculated by considering an isolated dimer with effective potential $V_{\text{eff},I} + V_{\text{eff},J}$. If this dimer is aligned with the z axis, the z-component of angular momentum is a good quantum number and matrix elements between basis functions with different values of the azimuthal quantum number m are zero. This reduces the number of non-zero two-center matrix elements substantially.

As an example, consider a dimer oriented along the z axis. One of the two atoms has a valence shell of p orbitals and the other a valence shell of d orbitals. For simplicity, we assume that the basis set is orthonormal, implying that the orbitals on the two atoms have been orthogonalized in some way. The non-zero one-center matrix elements involving orbitals on the first atom all have the same value, which we call V_p; the one-center matrix elements involving orbitals on the second atom are all equal to V_d. The non-zero hopping matrix elements linking the two atoms have only two possible values, $h_{pd\sigma}$ and $h_{pd\pi}$, corresponding to pairs of orbitals with $m = 0$ or $m = 1$. Since no p orbital has $m = \pm 2$, there are no non-zero hopping matrix elements with $m = \pm 2$, even though there are d orbitals with $m = \pm 2$ on the second atom. Thus, the electronic structure of the dimer is defined by just four numbers. Quantities such as V_p, V_d, $h_{pd\sigma}$, and $h_{pd\pi}$ are called Slater-Koster parameters [1].
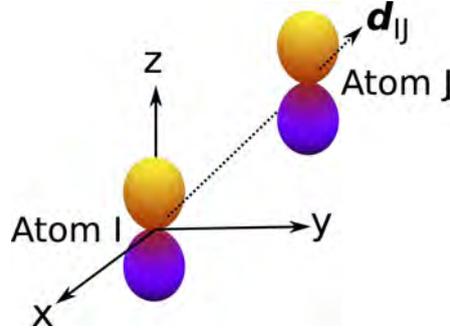
Fig. 5: *A two-center matrix element between p_z orbitals on atoms I and J separated by the vector $\boldsymbol{d}_{IJ} = \boldsymbol{d}_J - \boldsymbol{d}_I$. Each p_z orbital may be expressed as a linear combination of p_x, p_y and p_z orbitals quantized relative to the $\boldsymbol{d}_{IJ}$ axis, so the matrix element is a linear combination of the Slater-Koster parameters $h_{pp\pi}$ and $h_{pp\sigma}$.*

We have not yet worked out how to evaluate two-center Hamiltonian matrix elements for dimers not aligned with the global z axis. An example of this problem is shown in Fig. 5. The two p_z orbitals are neither parallel nor perpendicular to the dimer axis $\boldsymbol{d}_{IJ}$, so the two-center hopping matrix element between them is neither $h_{pp\sigma}$ (the value for two p orbitals pointing along $\boldsymbol{d}_{IJ}$) nor $h_{pp\pi}$ (the value for two p orbitals pointing perpendicular to $\boldsymbol{d}_{IJ}$). Fortunately, rotating a real spherical harmonic $\tilde{Y}_l^m$ always produces a linear combination of real spherical harmonics with the same value of l but different values of m. More precisely, if the operator $\hat{R}^{\boldsymbol{\omega}}$ rotates the function to which it is applied by ω radians about an axis parallel to the unit vector $\hat{\boldsymbol{\omega}}$, the rotated real spherical harmonic $\hat{R}^{\boldsymbol{\omega}}\tilde{Y}_l^m$ can be expressed as a linear combination of the $2l + 1$ unrotated real spherical harmonics with the same value of l:

$$\hat{R}^{\boldsymbol{\omega}}\tilde{Y}_l^m = \sum_{m'=-l}^{l} \tilde{D}_{m',m}^l(\boldsymbol{\omega})\,\tilde{Y}_l^{m'}. \tag{18}$$

This allows us to express the orbitals pictured in Fig. 5 as linear combinations of orbitals aligned with the dimer axis, and hence to express the two-center Hamiltonian and overlap matrix elements for the tilted dimer in terms of the Slater-Koster parameters. Slater and Koster [1] provide a convenient table expressing the two-center matrix elements of the rotated dimer in terms of the Slater-Koster parameters and the direction cosines of the dimer axis. Given the one-center Slater-Koster parameters for all atom types and the two-center Slater-Koster parameters for all pairs of atom types at all inter-atomic separations, one can use this table to write down the two-center tight-binding Hamiltonian for any molecule or solid built of those atoms.

2.2.6 Fitting and transferability

Semi-empirical tight-binding Hamiltonian and overlap matrix elements (if the model is non-orthogonal) are often fitted to bandstructures. This makes sense if individual electronic eigenvalues and eigenfunctions are the quantities of interest, as is the case, for example, in electronic transport calculations, but is not appropriate if the tight-binding model is to be used to calculate total energies or inter-atomic forces. In that case it is better to fit to total energies and/or forces

calculated for a variety of structures using a more accurate method such as DFT with a good basis set. The wider the range of local atomic environments included in the data set, the better the results. Large tabulations of fitted tight-binding parameters are available [19].

It would be impractical to refit the parameters of a tight-binding model for every different arrangement of the ions in a molecular dynamics simulation, so assumptions have to be made about how the matrix elements between nearby orbitals depend on ionic positions. The short range of the atomic-like basis functions, and the observation that the form of the potential in one region of a solid or molecule does not normally depend strongly on the positions of distant atoms, suggest that only the local ionic arrangement is important. It does not, however, imply that the mapping from ionic positions to matrix elements is simple. If the assumptions made in parametrizing a tight-binding model are wrong or inaccurate, it is likely to produce poor results whenever the local ionic arrangement is far from any of the arrangements included in the training set. In such cases we say that the tight-binding model is not "transferable".

In general, despite all the work that has been done, parametrizing and fitting semi-empirical tight-binding models remains a dark art. Some of the most successful attempts [20] are among the simplest and were constructed using very little data, while highly-fitted models often prove brittle and show poor transferability. The problem of constructing a transferable semi-empirical tight-binding model is similar in nature to the problem of constructing a transferable classical force field and leads to similar frustrations. Tight-binding models are better than force fields because they are properly quantum mechanical — but they are only an approximation. As we illustrate with a few examples below, semi-empirical tight-binding is at its best when used to build a qualitative understanding of chemical bonding.

2.3 Example semi-empirical tight-binding calculations

2.3.1 The hydrogen molecule

Two hydrogen atoms are held a distance d apart and approximated using a tight-binding model with a single atomic-like s orbital on each atom. The Hamiltonian and overlap matrices are

$$\boldsymbol{H} = \begin{pmatrix} V & h \\ h & V \end{pmatrix} \quad \text{and} \quad \boldsymbol{S} = \begin{pmatrix} 1 & s \\ s & 1 \end{pmatrix}. \tag{19}$$

The eigenvectors are

$$\boldsymbol{e}_{+} = \frac{1}{\sqrt{2(1+s)}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \quad \text{and} \quad \boldsymbol{e}_{-} = \frac{1}{\sqrt{2(1-s)}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}, \tag{20}$$

normalized such that

$$\boldsymbol{e}_{i}^{\dagger} \boldsymbol{S} \, \boldsymbol{e}_{j} = \delta_{ij}, \tag{21}$$

as is appropriate for a generalized eigenvalue problem. The corresponding eigenvalues are

$$\epsilon_{\pm} = \frac{V \pm h}{1 \pm s}. \tag{22}$$

It is reassuring to see the bonding and anti-bonding linear combinations of basis functions emerge naturally from the analysis.
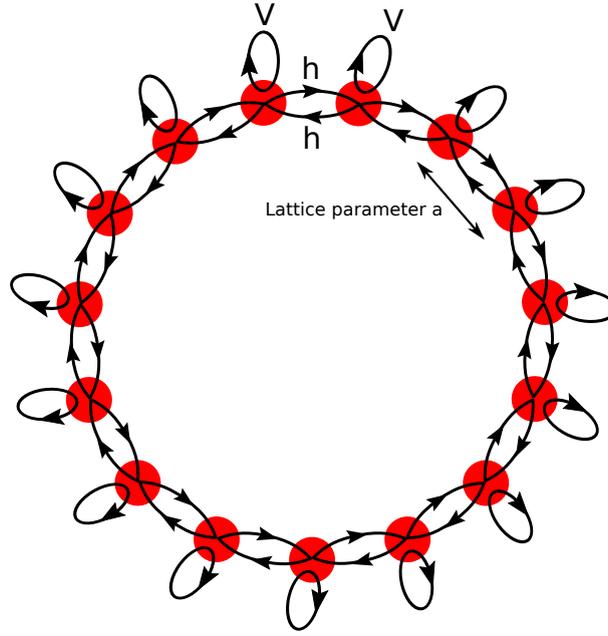
Fig. 6: *A schematic representation of the tight-binding Hamiltonian matrix of a ring of hydrogen atoms subject to periodic boundary conditions.*

2.3.2 Bandstructure of a ring of hydrogen atoms

Consider a chain of N hydrogen atoms subject to periodic boundary conditions (i.e., with the ends joined together to form a ring). A schematic representation of the Hamiltonian matrix is shown in the Fig. 6. As in the case of the H_2 molecule, there are on-site (diagonal) Hamiltonian matrix elements V and nearest-neighbor hopping matrix elements h. This time, however, we assume for simplicity that the basis set is orthonormal. We shall also assume, as usually turns out to be the case, that h is negative. The Hamiltonian is an $N \times N$ matrix with N large, so it looks as if it will be difficult to find the eigenvalues and eigenvectors. If we remember to use Bloch's theorem, however, the problem becomes simple.

A normalized Bloch-like linear combination of basis functions takes the form

$$|\psi_{k_p}\rangle = \frac{1}{\sqrt{N}} \sum_{n=0}^{N-1} |\phi_n\rangle \, e^{ik_p na} , \qquad (23)$$

where

$$k_p = \frac{2\pi p}{Na} \quad \text{with} \quad p = 0, 1, 2, \ldots, N-1, \qquad (24)$$

and a is the bond length. The values of k_p are chosen such that $|\psi_{k_p}\rangle$ satisfies the periodic boundary conditions: $\langle\phi_0|\psi_{k_p}\rangle = \langle\phi_N|\psi_{k_p}\rangle$. Since $\exp(ik_{p+N}na) = \exp(ik_p na)$ for any integer n, we lose nothing by restricting p to the range $0 \le p < N$.

Applying the projected Hamiltonian $\hat{H}^P = \sum_{m,n} |\phi_m\rangle H_{mn} \langle\phi_n|$ to the Bloch function $|\psi_{k_p}\rangle$
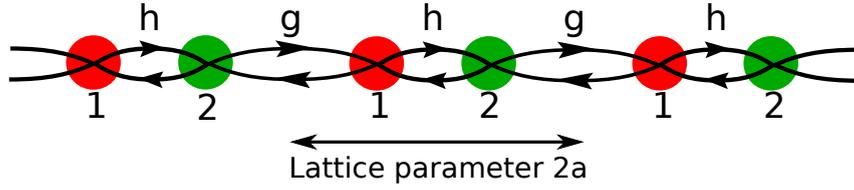
Fig. 7: *A schematic representation of the tight-binding Hamiltonian matrix of part of a large ring of diatomic molecules subject to periodic boundary conditions.*

gives

$$
\begin{aligned}
\hat{H}^P|\psi_{k_p}\rangle &= \frac{1}{\sqrt{N}} \sum_{n=0}^{N-1} \hat{H}^P|\phi_n\rangle \\
&= \frac{1}{\sqrt{N}} \sum_{n=0}^{N-1} \Big(V|\phi_n\rangle + h|\phi_{n-1}\rangle + h|\phi_{n+1}\rangle\Big) e^{ik_p na} \\
&= V\left(\frac{1}{\sqrt{N}} \sum_{n=0}^{N-1} |\phi_n\rangle e^{ik_p na}\right) + he^{ik_p a}\left(\frac{1}{\sqrt{N}} \sum_{n=0}^{N-1} |\phi_{n-1}\rangle e^{ik_p (n-1)a}\right) \\
&\qquad\qquad + he^{-ik_p a}\left(\frac{1}{\sqrt{N}} \sum_{n=0}^{N-1} |\phi_{n+1}\rangle e^{ik_p (n+1)a}\right).
\end{aligned}
\tag{25}
$$

Noting that $|\phi_{-1}\rangle \equiv |\phi_{n-1}\rangle$ and $|\phi_N\rangle \equiv |\phi_0\rangle$ because of the periodic boundary conditions, this simplifies to

$$
\hat{H}^P|\psi_{k_p}\rangle = \left[V + h(e^{ik_p a} + e^{-ik_p a})\right]|\psi_{k_p}\rangle,
\tag{26}
$$

showing that $|\psi_{k_p}\rangle$ is an eigenfunction of $\hat{H}^P$ with eigenvalue

$$
\epsilon(k_p) = V + 2h\cos(k_p a).
\tag{27}
$$

As the size N of the ring increases, the allowed values of k_p get closer and closer together and the cosinusoidal bandstructure of the infinite tight-binding ring is sampled more and more densely.

2.3.3 Bandstructure of a ring of diatomic molecules

The tight-binding model pictured in Fig. 7 has two orbitals per unit cell and produces two energy bands. There are N unit cells ($2N$ atoms) altogether and N inequivalent values of k consistent with the periodic boundary conditions. For simplicity we set the diagonal Hamiltonian matrix elements V_1 and V_2 to zero; the nearest-neighbor off-diagonal Hamiltonian matrix elements h and g (both of which are < 0) alternate along the chain.

Since we have two basis functions per unit cell, we can construct two Bloch functions at each allowed value of k:

$$
|\psi^{(1)}\rangle = \frac{1}{\sqrt{N}} \sum_n e^{ikn2a}|\phi_{n,1}\rangle, \qquad\qquad |\psi^{(2)}\rangle = \frac{1}{\sqrt{N}} \sum_n e^{ikn2a}|\phi_{n,2}\rangle,
$$
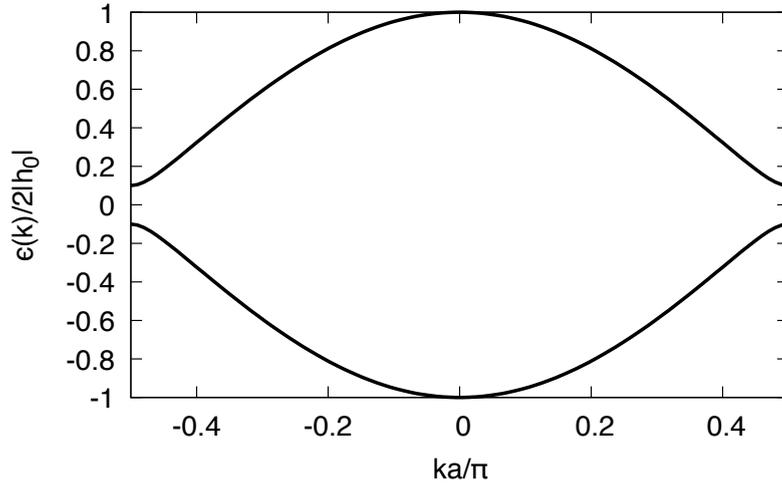
Fig. 8: *The bandstructure of the tight-binding ring of dimers in the limit as the number N of two-atom unit cells tends to infinity. There are two bands because there are two basis functions per unit cell.*

where $|\phi_{n,1}\rangle$ and $|\phi_{n,2}\rangle$ are the two basis functions in unit cell n. The unit cell now has length $2a$, so the Brillouin zone is $-\pi/(2a) \leq k < \pi/(2a)$. The corresponding vectors of orbital coefficients, $\boldsymbol{c}^{(1)}$ and $\boldsymbol{c}^{(2)}$, with components

$$c_{n,1}^{(1)} = \frac{1}{\sqrt{N}}e^{ikn2a}, \qquad c_{n,2}^{(1)} = 0,$$

and

$$c_{n,1}^{(2)} = 0, \qquad c_{n,2}^{(2)} = \frac{1}{\sqrt{N}}e^{ikn2a},$$

satisfy

$$\boldsymbol{H}\boldsymbol{c}^{(1)} = h\boldsymbol{c}^{(2)} + ge^{+ik2a}\boldsymbol{c}^{(2)},$$
$$\boldsymbol{H}\boldsymbol{c}^{(2)} = h\boldsymbol{c}^{(1)} + ge^{-ik2a}\boldsymbol{c}^{(1)},$$

where $\boldsymbol{H}$ is the $2N \times 2N$ Hamiltonian matrix. It follows that the linear combination $\boldsymbol{v} = \alpha_1\boldsymbol{c}^{(1)} + \alpha_2\boldsymbol{c}^{(2)}$ is an eigenvector of $\boldsymbol{H}$ if

$$\begin{pmatrix} 0 & h + ge^{-ik2a} \\ h + ge^{ik2a} & 0 \end{pmatrix} \begin{pmatrix} \alpha_1 \\ \alpha_2 \end{pmatrix} = \lambda \begin{pmatrix} \alpha_1 \\ \alpha_2 \end{pmatrix}.$$

The two energy eigenvalues $\epsilon_\pm(k)$ at wavevector k are the eigenvalues of this 2×2 matrix. Writing $h = (1 + \Delta)h_0$ and $g = (1 - \Delta)h_0$, some algebra shows that

$$\epsilon_\pm(k) = \pm 2|h_0|\sqrt{1 - (1 - \Delta^2)\sin^2(ka)}.$$

Fig. 8 shows the bandstructure in the case when $\Delta = 0.1$.
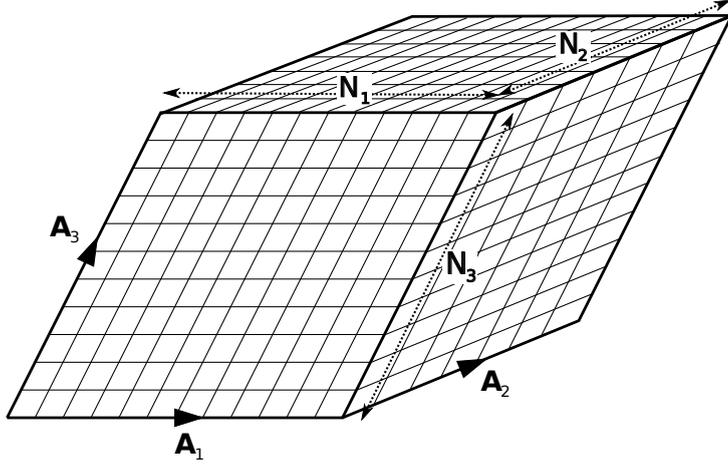
Fig. 9: *The $N_1 \times N_2 \times N_3$ parallelepiped supercell to which periodic boundary conditions are applied.*

2.3.4   Bandstructure of a face-centered-cubic solid

Consider a large but finite face-centered-cubic crystal consisting of a block of $N_1 \times N_2 \times N_3$ parallelepiped unit cells, as illustrated in Fig. 9. Apply periodic (*not* Bloch) boundary conditions, so that an electron leaving one face of the block immediately reappears at the equivalent point on the opposite face. The primitive Bravais lattice vectors are

$$\boldsymbol{A}_1 = \frac{a}{2}(0,1,1)\,, \qquad \boldsymbol{A}_2 = \frac{a}{2}(1,0,1)\,, \qquad \boldsymbol{A}_3 = \frac{a}{2}(1,1,0)\,, \qquad (28)$$

and the corresponding reciprocal vectors are

$$\boldsymbol{B}_1 = \frac{2\pi}{a}(-1,1,1)\,, \qquad \boldsymbol{B}_2 = \frac{2\pi}{a}(1,-1,1)\,, \qquad \boldsymbol{B}_3 = \frac{2\pi}{a}(1,1,-1)\,. \qquad (29)$$

The $N_1 N_2 N_3$ distinct $\boldsymbol{k}$ vectors consistent with the periodic boundary conditions are

$$\boldsymbol{k} = \frac{m_1}{N_1}\boldsymbol{B}_1 + \frac{m_2}{N_2}\boldsymbol{B}_2 + \frac{m_3}{N_3}\boldsymbol{B}_3 \quad \text{with} \quad 0 \le m_1 < N_1,\ \ 0 \le m_2 < N_2,\ \ 0 \le m_3 < N_3. \quad (30)$$

As in the previous examples, we approximate the system as an orthogonal tight-binding model with one atomic-like s orbital per atom. The diagonal matrix elements V_s are set to zero (defining the zero of energy) and the nearest-neighbor hopping matrix elements are equal to h. Matrix elements linking orbitals on more distant neighbors are assumed to be zero. The Bloch linear combinations of basis functions are

$$|\psi_{\boldsymbol{k}}\rangle = \frac{1}{\sqrt{N_1 N_2 N_3}} \sum_{\boldsymbol{d}} |\phi_{\boldsymbol{d}}\rangle\, e^{i\boldsymbol{k}\cdot\boldsymbol{d}}\,, \qquad (31)$$

where the sum is over the positions $\boldsymbol{d}$ of all $N_1 N_2 N_3$ atoms in the block and $|\phi_{\boldsymbol{d}}\rangle$ is the basis function on the atom at $\boldsymbol{d}$. Eq. (31) is a three-dimensional analogue of the one-dimensional Bloch linear combination used in Sec. 2.3.2.

Applying the projected Hamiltonian $\hat{H}^P = \sum_{\boldsymbol{d},\boldsymbol{d}'} |\phi_{\boldsymbol{d}}\rangle H_{\boldsymbol{d},\boldsymbol{d}'} \langle \phi_{\boldsymbol{d}'}|$ to the Bloch linear combination gives

$$
\begin{aligned}
\hat{H}^P|\psi_{\boldsymbol{k}}\rangle &= \frac{1}{\sqrt{N_1 N_2 N_3}} \sum_{\boldsymbol{d}} \hat{H}^P|\phi_{\boldsymbol{d}}\rangle e^{i\boldsymbol{k}\cdot\boldsymbol{d}} \\
&= \frac{1}{\sqrt{N_1 N_2 N_3}} \sum_{\boldsymbol{d}'} \sum_{\boldsymbol{d}} |\phi_{\boldsymbol{d}'}\rangle\langle \phi_{\boldsymbol{d}'}|\hat{H}^P|\phi_{\boldsymbol{d}}\rangle e^{i\boldsymbol{k}\cdot\boldsymbol{d}} \\
&= \frac{1}{\sqrt{N_1 N_2 N_3}} \sum_{\boldsymbol{d}'} |\phi_{\boldsymbol{d}'}\rangle e^{i\boldsymbol{k}\cdot\boldsymbol{d}'} \sum_{\boldsymbol{d}} \langle \phi_{\boldsymbol{d}'}|\hat{H}^P|\phi_{\boldsymbol{d}}\rangle e^{i\boldsymbol{k}\cdot(\boldsymbol{d}-\boldsymbol{d}')}.
\end{aligned}
\tag{32}
$$

The only non-zero contributions to the inner summation are those for which $\boldsymbol{d}$ is a nearest neighbor of $\boldsymbol{d}'$, in which case the matrix element is equal to h. The summation over all lattice vectors $\boldsymbol{d}$ may therefore be replaced by a summation over the positions of the 12 nearest neighbors of the atom at $\boldsymbol{d}'$. Denoting the vectors from the atom at $\boldsymbol{d}'$ (or any other lattice site) to its 12 nearest neighbors by $\boldsymbol{n}$, we obtain

$$
\hat{H}^P|\psi_{\boldsymbol{k}}\rangle = \frac{1}{\sqrt{N_1 N_2 N_3}} \sum_{\boldsymbol{d}'} |\phi_{\boldsymbol{d}'}\rangle e^{i\boldsymbol{k}\cdot\boldsymbol{d}'} \sum_{\boldsymbol{n}} h e^{i\boldsymbol{k}\cdot\boldsymbol{n}} = \left(h \sum_{\boldsymbol{n}} e^{i\boldsymbol{k}\cdot\boldsymbol{n}} \right) |\psi_{\boldsymbol{k}}\rangle
\tag{33}
$$

Just as for a ring of hydrogen atoms, the Bloch functions are automatically eigenvalues of the tight-binding Hamiltonian. This is generally the case when there is only one basis function per unit cell, since the translational symmetry is then sufficient to determine the energy eigenfunctions completely. The sum over the 12 nearest neighbors is easily evaluated to obtain

$$
\epsilon(\boldsymbol{k}) = 4h \left[\cos\left(\frac{k_y a}{2}\right) \cos\left(\frac{k_z a}{2}\right) + \cos\left(\frac{k_z a}{2}\right) \cos\left(\frac{k_x a}{2}\right) + \cos\left(\frac{k_x a}{2}\right) \cos\left(\frac{k_y a}{2}\right) \right].
$$

This simple expression provides an accurate description of the bandstructure of any face-centered-cubic crystal of weakly-interacting atoms with outermost s shells. All of the Noble gases except helium crystallize into face-centered cubic structures under sufficient pressure, and all have bandstructures of this form.

3 Tight-binding models and density-functional theory

3.1 Introduction

Section 2 showed how the tight-binding approximation can be used to find approximate solutions of one-particle Schrödinger equations of the form

$$
\left[-\frac{1}{2}\nabla^2 + V_{\mathrm{eff}}(\boldsymbol{r}) \right] \psi_i(\boldsymbol{r}) = \epsilon_i \psi_i(\boldsymbol{r}).
\tag{34}
$$

This is useful but by no means the end of the story, since tight-binding models are also used to describe how the total energy of a solid or molecule varies as the atoms move around [2, 3, 7, 9, 11, 12, 14, 15]. Any tight-binding model capable of providing a reliable account of the

structure-dependent total energy can be used as an engine for the calculation of the inter-atomic forces (gradients of the total energy with respect to atomic positions) required for quantum molecular dynamics simulations. Tight-binding quantum molecular dynamics simulations are less accurate than their DFT equivalents but require much less computer power.

If one wishes to describe total energies, calculating the electronic eigenvalues ϵ_i of the occupied valence states is not sufficient [21]. The total energy also includes another term that represents, roughly, the repulsive interaction between the ionic cores:

$$E_{\text{total}}^{\text{TB}}(\boldsymbol{d}) = \sum_{i \text{ occ}} \epsilon_i(\boldsymbol{d}) + E_{\text{ion-ion}}(\boldsymbol{d}), \tag{35}$$

where $\boldsymbol{d} \equiv \{\boldsymbol{d}_1, \boldsymbol{d}_2, \ldots, \boldsymbol{d}_{N_I}\}$ is shorthand for the set of all ionic positions. (The dependence of the electronic eigenvalues ϵ_i on $\boldsymbol{d}$ arises via the position dependence of the Hamiltonian and overlap matrix elements.) The ion-ion interaction energy $E_{\text{ion-ion}}(\boldsymbol{d})$ must also be parametrized and/or fitted and is often but not always assumed to be pairwise in form:

$$E_{\text{ion-ion}}(\boldsymbol{d}) = \sum_{I > J} V_{\text{ion-ion}}^{\text{pair}}(\boldsymbol{d}_I - \boldsymbol{d}_J), \tag{36}$$

where the sum is over all pairs I and J of ions and $\boldsymbol{d}_I$ and $\boldsymbol{d}_J$ are the corresponding ionic positions.

The form of Eq. (35) is reminiscent of the expression for the total energy in Hohenberg-Kohn-Sham DFT,

$$E = \sum_{i \text{ occ}} \epsilon_i - \int V_{\text{KS}}([n], \boldsymbol{r}) n(\boldsymbol{r}) \, d^3r + \int V_{\text{nuc}}(\boldsymbol{r}) n(\boldsymbol{r}) \, d^3r + \frac{1}{2} \iint \frac{n(\boldsymbol{r}) n(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} \, d^3r' d^3r + E_{xc}[n] + E_{nn}, \tag{37}$$

where $n(\boldsymbol{r})$ is the electron number density and the eigenvalues are solutions of the Kohn-Sham equation, which looks like Eq. (34) with a density-dependent effective potential of the form:

$$V_{\text{KS}}([n], \boldsymbol{r}) = V_{\text{nuc}}(\boldsymbol{r}) + \int \frac{n(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} d^3r' + V_{xc}([n], \boldsymbol{r}). \tag{38}$$

The first term on the right-hand side of Eq. (38) is the potential exerted on the electrons by the classical, point-like nuclei; the second, known as the Hartree term, is the Coulomb potential of the electron charge cloud; and the third is the exchange-correlation potential, which is discussed below. The second term on the right-hand side of Eq. (37) cancels the potential energy contribution to the sum of energy eigenvalues, leaving only the kinetic energy contribution; the third, fourth and fifth terms add the energy of interaction between the electrons and nuclei, the Coulomb interaction energy of the electronic charge cloud, and the exchange-correlation energy. The final term is the classical Coulomb interaction energy of the nuclei with each other. A recap of the basics of DFT is given in Sec. 3.2 below. For the time being, we note only that the DFT total-energy expression, which experience has shown is usually very accurate, consists of a sum of eigenvalues and additional "ion-ion repulsion" terms. This looks quite like the tight-binding total energy expression, except that: (i) the DFT ion-ion repulsion terms

are density dependent and not obviously simple or pairwise; and (ii) the Kohn-Sham effective potential depends on the electron density $n(\boldsymbol{r})$, which in turn depends on the eigenfunctions via $n(\boldsymbol{r}) = \sum_{i \text{ occ}} |\psi_i(\boldsymbol{r})|^2$.

The dependence of the Kohn-Sham potential on the wavefunctions obtained by solving the Kohn-Sham equation means that an iterative method of solution is required. The first step is to guess an input electron density $n^{\text{in}}(\boldsymbol{r})$, which might perhaps be a superposition of atomic densities. The corresponding Kohn-Sham potential $V_{\text{KS}}([n^{\text{in}}], \boldsymbol{r})$ can then be calculated and the Kohn-Sham equation solved to find the output wavefunctions and hence the output density $n^{\text{out}}(\boldsymbol{r}) = \sum_{i \text{ occ}} |\psi_i^{\text{out}}(\boldsymbol{r})|^2$. The input and output densities differ in general, so the next step is to adjust the input density to try to reduce the difference between the input and output densities. After an iterative series of adjustments, a "self-consistent" electron density $n_0(\boldsymbol{r})$ is obtained, for which the wavefunctions $\psi_{0i}(\boldsymbol{r})$ obtained by solving the Kohn-Sham equation with input potential $V_{\text{KS}}([n_0], \boldsymbol{r})$ regenerate $n_0(\boldsymbol{r})$ exactly. In tight-binding total energy calculations, by contrast, the Schrödinger equation only has to be solved once and no self-consistency is required.

The aim of the rest of this section is to explain the link between DFT and tight-binding theory. Can we derive a non-selfconsistent tight-binding model with a simple ion-ion repulsion term from the much more complicated self-consistent formalism of DFT?

3.2   Review of density-functional theory

Density-functional theory [22, 23] looks like a mean-field theory, but is remarkable because it provides an exact mapping from a system of interacting electrons to a system of non-interacting electrons moving in an effective potential that depends on the electron density. Solving the self-consistent non-interacting problem gives, in principle, the *exact* interacting ground-state energy E_0 and electron density $n_0(\boldsymbol{r})$ for any given arrangement of the nuclei. The success of DFT, which appears to be a theory of non-interacting electrons but in fact describes a system of interacting electrons, in part explains the success of the "standard model" of a solid as an assembly of non-interacting electrons moving in a fixed external potential.

3.2.1   Preliminaries

The N-electron eigenfunctions $\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)$ of any finite collection of atoms satisfy the many-electron Schrödinger equation:

$$\left(-\frac{1}{2} \sum_i \nabla_i^2 + \sum_{i>j} \frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} - \sum_i \sum_I \frac{Z_I}{|\boldsymbol{r}_i - \boldsymbol{d}_I|} + \sum_{I>J} \frac{Z_I Z_J}{|\boldsymbol{d}_I - \boldsymbol{d}_J|} \right) \Psi = E\Psi, \qquad (39)$$

where $\boldsymbol{r}_i$ is the position of electron i and Z_I is the atomic number of atom I at position $\boldsymbol{d}_I$. For simplicity, we shorten this to

$$\left(\hat{T} + \hat{V}_{\text{ee}} + \hat{V}_{\text{en}} + E_{\text{nn}} \right) \Psi = E\Psi. \qquad (40)$$

We are working within the Born-Oppenheimer approximation and treating the nuclei as stationary and classical, so the nuclear positions d_I and nuclear-nuclear Coulomb interaction energy E_{nn} are regarded as constants when solving the electronic problem.

The central quantity in DFT is the electron (number) density $n(\boldsymbol{r})$, the operator for which is

$$\hat{n}(\boldsymbol{r}) = \sum_i^N \delta(\boldsymbol{r} - \boldsymbol{r}_i). \tag{41}$$

Since

$$\hat{V}_{en} = \sum_i^N V_{nuc}(\boldsymbol{r}_i) = \int V_{nuc}(\boldsymbol{r}) \sum_i^N \delta(\boldsymbol{r} - \boldsymbol{r}_i)\, d^3r, \tag{42}$$

the electron-nucleus interaction operator (or any other one-electron potential energy term) can be written in terms of the electron density operator:

$$\hat{V}_{en} = \int V_{nuc}(\boldsymbol{r})\, \hat{n}(\boldsymbol{r})\, d^3r. \tag{43}$$

Note that $\boldsymbol{r}$ in this equation is a simple vector, not an operator; the electron position operators $\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N$ are buried in the definition of $\hat{n}(\boldsymbol{r})$. Taking an expectation value of Eq. (43) gives the obvious result:

$$\langle \Psi | \hat{V}_{en} | \Psi \rangle = \int V_{nuc}(\boldsymbol{r}) \langle \Psi | \hat{n}(\boldsymbol{r}) | \Psi \rangle\, d^3r = \int V_{nuc}(\boldsymbol{r}) n(\boldsymbol{r})\, d^3r. \tag{44}$$

3.2.2 The energy functional

The first step in any derivation of DFT is to show that there exists a functional, $E[n]$, of the electron number density $n(\boldsymbol{r})$, which takes its minimum value, equal to the ground-state energy E_0, when the density is the ground-state density $n_0(\boldsymbol{r})$. Levy [24] manages this by giving an explicit construction of such a functional:

$$E[n] = \min_{\Psi \to n} \langle \Psi | \hat{H} | \Psi \rangle = \min_{\Psi \to n} \langle \Psi | \hat{T} + \hat{V}_{ee} + \hat{V}_{en} + E_{nn} | \Psi \rangle. \tag{45}$$

In words: given an electron density $n(\boldsymbol{r})$, the functional $E[n]$ is evaluated by checking all possible normalized antisymmetric N-electron wavefunctions which give that density to find the one that minimizes $\langle \Psi | \hat{H} | \Psi \rangle$. This minimum value is the value assigned to the functional at the density $n(\boldsymbol{r})$. It can be shown that it is possible to find at least one N-electron wavefunction corresponding to any reasonable density $n(\boldsymbol{r})$, so the constrained search always produces a value.

The variational principle guarantees that the minimum value of $E[n]$ occurs when $n(\boldsymbol{r})$ is equal to the ground-state density $n_0(\boldsymbol{r})$. The optimal wavefunction Ψ is then the ground state Ψ_0, and the value of the functional is the ground-state energy:

$$E[n_0] = \min_{\Psi \to n_0} \langle \Psi | \hat{H} | \Psi \rangle = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle = E_0\,. \tag{46}$$

Since E_{nn} is a constant, and since the expectation value of $\hat{V}_{\text{en}}$ gives the same result,

$$\langle \Psi | \hat{V}_{\text{en}} | \Psi \rangle = \int V_{\text{en}}(\boldsymbol{r}) n(\boldsymbol{r}) \, d^3 r, \tag{47}$$

for *all* wavefunctions Ψ yielding the density $n(\boldsymbol{r})$, the total-energy functional may be written in the form

$$E[n] = \min_{\Psi \to n} \langle \Psi | \hat{T} + \hat{V}_{\text{ee}} | \Psi \rangle + \int V_{\text{en}}(\boldsymbol{r}) n(\boldsymbol{r}) \, d^3 r + E_{\text{nn}} = F[n] + \int V_{\text{en}}(\boldsymbol{r}) n(\boldsymbol{r}) \, d^3 r + E_{\text{nn}}, \tag{48}$$

where the second equality defines $F[n]$.

The definition of $F[n]$ makes no reference to the positions of the nuclei, so its value depends on the electron density $n(\boldsymbol{r})$ only. It is thus a *universal* functional: given an input density $n(\boldsymbol{r})$, the value of $F[n]$ is fixed regardless of the nuclear charges or positions. (Remember that functionals such as $E[n]$ and $F[n]$ are defined for *all* reasonable input densities $n(\boldsymbol{r})$; the density that minimizes $E[n]$ depends on the arrangement of the ions, but that is a separate issue.) Since the functional $F[n]$ is the same in all solids, atoms and molecules, it could in principle be calculated once and for all.

3.2.3 Contributions to the energy functional

If, given a density $n(\boldsymbol{r})$, we could easily evaluate $E[n]$, the many-electron problem would be solved: all that we would have to do to find the ground-state density and energy would be to vary $n(\boldsymbol{r})$ until the functional reached a minimum. Unfortunately, but not unexpectedly, evaluating the functional is equivalent to solving the full N-body problem and is out of the question. We therefore have to approximate.

To make approximating the energy functional easier, it helps to identify some of the contributions to $F[n]$. Since the definition of $F[n]$ involves an expectation value of the electron-electron interaction, one obvious contribution is the Hartree energy:

$$E_{\text{H}}[n] = \frac{1}{2} \iint \frac{n(\boldsymbol{r}) n(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} d^3 r \, d^3 r'. \tag{49}$$

Another large and easily recognizable contribution is the kinetic energy of the interacting electrons. Although this is hard to evaluate, we can work out the kinetic energy $T_s[n]$ of a system of non-interacting electrons with ground-state density $n(\boldsymbol{r})$. There is no reason to think that $T_s[n]$ is the same as the kinetic energy of the interacting electrons, but it is of the same order of magnitude and relatively easy to calculate.

One way to work out $T_s[n]$ is to choose a non-interacting Hamiltonian, $-\frac{1}{2}\nabla^2 + V_{\text{eff}}(\boldsymbol{r})$, solve the Schrödinger equation

$$\left[-\frac{1}{2}\nabla^2 + V_{\text{eff}}(\boldsymbol{r}) \right] \psi_i(\boldsymbol{r}) = \epsilon_i \psi_i(\boldsymbol{r}), \tag{50}$$

and occupy first N eigenfunctions to obtain the corresponding electron density

$$n(\boldsymbol{r}) = \sum_{i \text{ occ}} |\psi_i(\boldsymbol{r})|^2. \tag{51}$$

$T_s[n]$ is then given by:

$$T_s[n] = \sum_{i \text{ occ}} \int \psi_i^*(\boldsymbol{r}) \left(-\frac{1}{2}\nabla^2 \right) \psi_i(\boldsymbol{r}) \, d^3r = \sum_{i \text{ occ}} \epsilon_i - \int V_{\text{eff}}(\boldsymbol{r}) n(\boldsymbol{r}) \, d^3r \,. \tag{52}$$

The drawback of this technique is that it produces the value of $T_s[n]$ at the density $n(\boldsymbol{r})$ obtained by solving the Schrödinger equation. If you require $T_s[n]$ at a given density $n(\boldsymbol{r})$, it is necessary to vary the input potential $V_{\text{eff}}(\boldsymbol{r})$ until the output density $\sum_{i \text{ occ}} |\psi_i(\boldsymbol{r})|^2$ is equal to $n(\boldsymbol{r})$. This may not even be possible — not every density $n(\boldsymbol{r})$ is the ground-state density of a non-interacting system — although it rarely if ever poses a problem in practice.

So far, then, we have identified two contributions that we believe should make up a large part of $F[n]$. The next step is to write

$$F[n] = T_s[n] + E_{\text{H}}[n] + E_{\text{xc}}[n], \tag{53}$$

or, equivalently,

$$E[n] = T_s[n] + \int V_{\text{nuc}}(\boldsymbol{r}) n(\boldsymbol{r}) \, d^3r + E_{\text{H}}[n] + E_{\text{xc}}[n] + E_{\text{nn}}. \tag{54}$$

The terms we have identified have been written explicitly, and $E_{\text{xc}}[n]$, known as the exchange and correlation energy, is a "rubbish" term to take care of the rest of $F[n]$. Like $F[n]$, the Hartree energy $E_{\text{H}}[n]$ and the non-interacting kinetic energy $T_s[n]$ are universal functionals of the electron density and could, in principle, be calculated once and for all. Since

$$E_{\text{xc}}[n] = F[n] - T_s[n] - E_{\text{H}}[n], \tag{55}$$

it follows that the exchange-correlation functional $E_{\text{xc}}[n]$ is also universal.

Given an electron density $n(\boldsymbol{r})$, the non-interacting kinetic energy, the Hartree energy, the electron-nuclear interaction energy, and the nuclear-nuclear interaction energy are all easily obtained. The only difficult term is the unknown universal functional $E_{\text{xc}}[n]$. This includes all of the complicated parts of the many-body problem and has to be approximated. The surprising accuracy of simple approximations to $E_{xc}[n]$ is the reason DFT is so useful. The question of how to construct good approximate exchange-correlation functionals is fascinating but too complicated to discuss here. For our purposes, it is sufficient to assume that good approximations exist and can be evaluated easily.

3.2.4 Minimization of the energy functional

We now know how to evaluate all the terms in the energy functional

$$E[n] = T_s[n] + E_{\text{en}}[n] + E_{\text{H}}[n] + E_{\text{nn}} + E_{\text{xc}}[n]. \tag{56}$$

To calculate the exact interacting ground-state density $n_0(\boldsymbol{r})$ (and hence the exact ground-state energy E_0), we have to find the density that minimizes $E[n]$ subject to the normalization constraint $\int n(\boldsymbol{r})\,d^3r = N$. Mathematically, the ground-state density is determined by the stationarity condition,

$$\delta E = \int \frac{\delta E[n]}{\delta n(\boldsymbol{r})}\,\delta n(\boldsymbol{r})\,d^3r = 0, \tag{57}$$

which must hold for all density variations $\delta n(\boldsymbol{r})$ that integrate to zero.

The variations of the electron-nuclear and Hartree terms are easy to find:

$$\delta E_{\mathrm{en}} = \delta \left(\int V_{\mathrm{nuc}}(\boldsymbol{r}) n(\boldsymbol{r})\,d^3r \right) = \int V_{\mathrm{nuc}}(\boldsymbol{r})\,\delta n(\boldsymbol{r})\,d^3r, \tag{58}$$

$$\delta E_{\mathrm{H}} = \int \left(\int \frac{n(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}\,d^3r' \right) \delta n(\boldsymbol{r})\,d^3r = \int V_H([n],\boldsymbol{r})\,\delta n(\boldsymbol{r})\,d^3r, \tag{59}$$

where $V_H([n],\boldsymbol{r})$ is the Hartree potential mentioned earlier. The variation of the exchange-correlation energy,

$$\delta E_{\mathrm{xc}} = \int \frac{\delta E_{\mathrm{xc}}}{\delta n(\boldsymbol{r})}\,\delta n(\boldsymbol{r})\,d^3r = \int V_{\mathrm{xc}}([n],\boldsymbol{r})\,\delta n(\boldsymbol{r})\,d^3r \tag{60}$$

defines the exchange-correlation potential $V_{\mathrm{xc}}([n],\boldsymbol{r})$, which is easy enough to work out given a simple approximate exchange-correlation functional.

The variation of the kinetic energy functional can be found by returning to Eqs. (50), (51), and (52). Suppose that the input potential changes from V_{eff} to $V_{\mathrm{eff}} + \delta V_{\mathrm{eff}}$, causing the output density — the density at which T_s is calculated — to change from n to $n + \delta n$. Using first-order perturbation theory, the sum of the occupied one-electron eigenvalues changes by

$$\sum_{i\,\mathrm{occ}} \delta\epsilon_i = \sum_{i\,\mathrm{occ}} \int \psi_i^*(\boldsymbol{r})\,\delta V_{\mathrm{eff}}(\boldsymbol{r})\,\psi_i(\boldsymbol{r})\,d^3r = \int n(\boldsymbol{r})\,\delta V_{\mathrm{eff}}(\boldsymbol{r})\,d^3r. \tag{61}$$

Hence

$$\begin{aligned}
\delta T_s &= \delta \left[\sum_{i\,\mathrm{occ}} \epsilon_i - \int V_{\mathrm{eff}}(\boldsymbol{r}) n(\boldsymbol{r})\,d^3r \right] \\
&= \int n(\boldsymbol{r})\,\delta V_{\mathrm{eff}}(\boldsymbol{r})\,d^3r - \int \left[n(\boldsymbol{r})\,\delta V_{\mathrm{eff}}(\boldsymbol{r}) + V_{\mathrm{eff}}(\boldsymbol{r})\,\delta n(\boldsymbol{r}) \right] d^3r \\
&= -\int V_{\mathrm{eff}}(\boldsymbol{r})\,\delta n(\boldsymbol{r})\,d^3r \,.
\end{aligned} \tag{62}$$

By combining the variations of each term, we can now write down the Euler-Lagrange equation that determines the minimum of the total energy functional:

$$\begin{aligned}
\delta E &= \delta T_s + \delta E_{\mathrm{en}} + \delta E_{\mathrm{H}} + \delta E_{\mathrm{xc}} \\
&= \int \Big(-V_{\mathrm{eff}}(\boldsymbol{r}) + V_{\mathrm{nuc}}(\boldsymbol{r}) + V_H([n],\boldsymbol{r}) + V_{\mathrm{xc}}([n],\boldsymbol{r}) \Big) \delta n(\boldsymbol{r})\,d^3r = 0.
\end{aligned} \tag{63}$$

Because of the constraint of normalization conservation,

$$\int \delta n(\boldsymbol{r}) \, d^3 r = 0, \tag{64}$$

the $\boldsymbol{k} = \boldsymbol{0}$ Fourier component of $-V_{\text{eff}} + V_{\text{nuc}} + V_{\text{H}} + V_{\text{xc}}$ is not fixed by Eq. (63). All other Fourier components must be zero, however, and hence

$$V_{\text{eff}}(\boldsymbol{r}) = V_{\text{nuc}}(\boldsymbol{r}) + V_{\text{H}}([n], \boldsymbol{r}) + V_{\text{xc}}([n], \boldsymbol{r}) + \text{const.} = V_{\text{KS}}([n], \boldsymbol{r}) + \text{const.} \tag{65}$$

The value of the constant has no effect on the calculation of $T_s[n]$ (which is the only purpose of V_{eff}), so we set it to zero.

Let us think about the meaning of Eq. (65). The total energy functional is minimized when the potential $V_{\text{eff}}(\boldsymbol{r})$ appearing in the non-interacting Schrödinger equation with ground-state density $n(\boldsymbol{r})$ is exactly equal to $V_{\text{KS}}([n], \boldsymbol{r}) = V_{\text{nuc}}(\boldsymbol{r}) + V_{\text{H}}([n], \boldsymbol{r}) + V_{\text{xc}}(]n], \boldsymbol{r})$. Since V_{H} and V_{xc} depend on the electron density, this is the self-consistency condition discussed in Sec. 3.1: the potential occurring in the non-interacting Schrödinger equation is determined by the ground-state electron density obtained by solving that equation.

3.2.5   Expressions for the DFT total energy

Once the ground-state density $n_0(\boldsymbol{r})$ and the corresponding effective potential $V_{\text{KS}}([n_0], \boldsymbol{r})$ and one-electron wavefunctions $\psi_{0i}(\boldsymbol{r})$ have been found, the total ground-state energy is given by

$$E[n_0] = T_s[n_0] + E_{\text{en}}[n_0] + E_H[n_0] + E_{\text{xc}}[n_0] + E_{\text{nn}}. \tag{66}$$

Since

$$T_s[n_0] = \sum_{i \text{ occ}} \epsilon_{0i} - \int V_{\text{KS}}([n_0], \boldsymbol{r}) n_0(\boldsymbol{r}) \, d^3 r, \tag{67}$$

the ground-state energy may also be written as

$$E = \sum_{i \text{ occ}} \epsilon_{0i} - \int V_{\text{KS}}([n_0], \boldsymbol{r}) n_0(\boldsymbol{r}) \, d^3 r + E_{\text{en}}[n_0] + E_H[n_0] + E_{\text{xc}}[n_0] + E_{\text{nn}}. \tag{68}$$

The total ground-state energy is not just the sum of the one-electron eigenvalues, as might be expected, but includes additional density-dependent terms. These we referred to earlier as the ion-ion interaction terms, but they are more often called the double-counting-correction terms. This name is appropriate because $V_{\text{KS}}([n_0], \boldsymbol{r})$ includes the Hartree potential,

$$V_{\text{H}}([n_0], \boldsymbol{r}) = \int \frac{n_0(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} d^3 r', \tag{69}$$

so the sum of self-consistent eigenvalues includes the Hartree energy twice:

$$\int V_{\text{H}}([n_0], \boldsymbol{r}) n_0(\boldsymbol{r}) d^3 r = \iint \frac{n_0(\boldsymbol{r}) n_0(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} = 2 E_H[n_0]. \tag{70}$$

The double-counting corrections remedy this problem.

3.3 Density-functional theory without self-consistency

Although DFT calculations require iteration to self-consistency, most tight-binding total energy calculations do not. To help relate the tight-binding approximation to DFT, we now ask whether DFT calculations can also be made non-selfconsistent. The idea is to guess the ground-state density $n_0(\boldsymbol{r})$ and perhaps also the ground-state Kohn-Sham potential $V_{\mathrm{KS}}([n_0], \boldsymbol{r})$, and evaluate the total energy functional using these guesses. Since the guesses are inputs to the non-selfconsistent calculation, we call then $n^{\mathrm{in}}(\boldsymbol{r})$ and $V_{\mathrm{eff}}^{\mathrm{in}}(\boldsymbol{r})$ from now on. To improve the accuracy of the approximate energies obtained, we insist that the expression evaluated to obtain the approximate total energy must be exact when the input density and potential are exact and stationary with respect to small variations of the input density and/or potential about the exact ground state. The errors in energies evaluated are then of second or higher order in $n^{\mathrm{in}}(\boldsymbol{r}) - n_0(\boldsymbol{r})$ and $V_{\mathrm{eff}}^{\mathrm{in}}(\boldsymbol{r}) - V_{\mathrm{KS}}([n_0], \boldsymbol{r})$, which we hope are small.

DFT is already a variational theory, in that the total energy functional $E[n]$ is minimized at the ground-state density: if the guessed density is $n^{\mathrm{in}}(\boldsymbol{r}) = n_0(\boldsymbol{r}) + \Delta n(\boldsymbol{r})$, the error in the total energy is positive and of order $(\Delta n)^2$. The standard DFT functional is difficult to work with, however, because the evaluation of $T_s[n^{\mathrm{in}}]$ requires the potential $V_{\mathrm{eff}}(\boldsymbol{r})$ for which n^{in} is the non-interacting ground-state density. Finding this potential requires a self-consistency cycle no easier than that appearing in an ordinary self-consistent DFT calculation.

Another option is to guess the input potential $V_{\mathrm{eff}}^{\mathrm{in}}(\boldsymbol{r})$, solve the Kohn-Sham equation once non-selfconsistently to obtain the corresponding one-electron eigenfunctions and output density, and call the output density $n^{\mathrm{out}}(\boldsymbol{r})$. At that point we have all of the information required to evaluate

$$E[n^{\mathrm{out}}] = T_s[n^{\mathrm{out}}] + E_{en}[n^{\mathrm{out}}] + E_H[n^{\mathrm{out}}] + E_{\mathrm{xc}}[n^{\mathrm{out}}] + E_{nn} \tag{71}$$

without self-consistent cycling. The drawback of this approach is that, even though $V_{\mathrm{eff}}^{\mathrm{in}}(\boldsymbol{r})$ may have a simple form — it could, for example, be a superposition of spherical atomic-like potentials as assumed in many tight-binding models — the output density $n^{\mathrm{out}}(\boldsymbol{r})$ will not normally be simple and the double-counting correction terms will be far from pairwise. The link between DFT and tight binding remains elusive.

3.3.1 General variational formulation of density-functional theory

The derivation of density functionals better adapted for use in non-selfconsistent calculations is made easier by starting from a very general variational formulation of DFT first described in the form used here by Haydock in 1998 [21].

Consider the following functional of $n(\boldsymbol{r})$, $V_{\mathrm{eff}}(\boldsymbol{r})$, and $\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)$, regarded as independent functions:

$$E[n, V_{\mathrm{eff}}, \Psi] = \langle \Psi | \left(\hat{T} + \int V_{\mathrm{eff}}(\boldsymbol{r}) \hat{n}(\boldsymbol{r}) \, d^3 r \right) | \Psi \rangle - \int V_{\mathrm{eff}}(\boldsymbol{r}) n(\boldsymbol{r}) \, d^3 r + G[n], \tag{72}$$

where

$$G[n] = \int V_{\mathrm{nuc}}(\boldsymbol{r}) n(\boldsymbol{r}) \, d^3 r + E_{\mathrm{H}}[n] + E_{\mathrm{xc}}[n] + E_{nn} \tag{73}$$

is shorthand for the sum of all Coulomb and exchange-correlation contributions to the total energy functional. The Kohn-Sham potential $V_{\text{KS}}([n], \boldsymbol{r})$ corresponding to density $n(\boldsymbol{r})$ is the functional derivative of $G[n]$:

$$V_{\text{KS}}([n], \boldsymbol{r}) = \frac{\delta G}{\delta n(\boldsymbol{r})}. \tag{74}$$

We seek the stationary points of $E[n, V_{\text{eff}}, \Psi]$ subject to the normalization constraints $\langle \Psi | \Psi \rangle = 1$ and $\int n(\boldsymbol{r}) d^3 r = N$. Since $\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)$ and $n(\boldsymbol{r})$ are independent functions in this approach, the two constraints are also independent.

The problem of finding the stationary points of $\langle \Psi | \hat{H} | \Psi \rangle$ subject to $\langle \Psi | \Psi \rangle = 1$ is equivalent to solving the Schrödinger equation $\hat{H}\Psi = E\Psi$, where E is a Lagrange multiplier for the constraint. The variations of $E[n, V_{\text{eff}}, \Psi]$ with respect to $n(\boldsymbol{r})$ and $V_{\text{eff}}(\boldsymbol{r})$ are easy to work out [note that varying the function $n(\boldsymbol{r})$ has no effect on the operator $\hat{n}(\boldsymbol{r})$], leading to the three Euler-Lagrange equations:

$$-V_{\text{eff}}(\boldsymbol{r}) + V_{\text{KS}}([n], \boldsymbol{r}) = \mu, \tag{75}$$

$$\langle \Psi | \hat{n}(\boldsymbol{r}) | \Psi \rangle - n(\boldsymbol{r}) = 0, \tag{76}$$

$$\left(\hat{T} + \int V_{\text{eff}}(\boldsymbol{r}) \hat{n}(\boldsymbol{r}) \right) | \Psi \rangle = E_{\text{non-int}} | \Psi \rangle, \tag{77}$$

where μ is a Lagrange multiplier for the density normalization constraint. The Lagrange multiplier for the wavefunction normalization constraint has been called $E_{\text{non-int}}$ to avoid confusion with the energy functional itself. All three Euler-Lagrange equations must be satisfied at any stationary point of $E[n, V_{\text{eff}}, \Psi]$.

The remarkable feature of these three equations is that they are fully equivalent to the equations of self-consistent DFT. The first says that the effective one-electron potential must equal the Kohn-Sham potential to within an arbitrary constant μ; this is the DFT self-consistency condition. The second says that $\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)$ must generate the one-electron density $n(\boldsymbol{r})$, just as in the Levy definition of the total energy functional. The third and final Euler-Lagrange equation says that the wavefunction Ψ must be an eigenfunction of the non-interacting Schrödinger equation

$$\sum_{i=1}^{N} \left(-\frac{1}{2} \nabla_i^2 + V_{\text{eff}}(\boldsymbol{r}_i) \right) \Psi = E_{\text{non-int}} \Psi, \tag{78}$$

which separates into N one-electron equations:

$$\left(-\frac{1}{2} \nabla^2 + V_{\text{eff}}(\boldsymbol{r}) \right) \psi_i(\boldsymbol{r}) = \epsilon_i[V_{\text{eff}}] \, \psi_i(\boldsymbol{r}). \tag{79}$$

If follows that the wavefunction Ψ appearing in the definition of the general density functional is single Slater determinant of the one-electron eigenfunctions used to calculate the non-interacting kinetic energy; it is not the physical many-electron wavefunction. If $E[n, V_{\text{eff}}, \Psi]$ is stationary with respect to variations of n and V_{eff} and minimized with respect to Ψ, the equations of DFT are fully satisfied and $E[n, V_{\text{eff}}, \Psi]$ is the ground-state energy of the interacting system.

Since $E[n, V_{\text{eff}}, \Psi]$ is stationary about the self-consistent DFT solution, we can replace n, V_{eff}, and Ψ by three *independent* guesses, n^{in}, $V_{\text{eff}}^{\text{in}}$ and Ψ^{in}, safe in the knowledge that $\Delta E = E[n^{\text{in}}, V_{\text{eff}}^{\text{in}}, \Psi^{\text{in}}] - E[n_0, V_{\text{KS}}[n_0], \Psi_0)$ is a quadratic form in the quantities $n^{\text{in}} - n_0$, $V_{\text{eff}}^{\text{in}} - V_{\text{KS}}[n_0]$, and $\Psi^{\text{in}} - \Psi_0$. If these are all small, the error in the calculated energy should be even smaller.

3.3.2 The Harris functional

The general variational formulation of DFT is a little too general to be useful in practice, but serves as a good starting point for deriving simpler density functionals. If we start by carrying out the constrained minimization with respect to Ψ to find the one-electron eigenvalues and eigenfunctions corresponding to the input potential V_{eff}, we obtain a functional of n and V_{eff} only:

$$E_{\text{GHF}}[n, V_{\text{eff}}] = \sum_{i \text{ occ}} \epsilon_i[V_{\text{eff}}] - \int V_{\text{eff}}(\boldsymbol{r}) n(\boldsymbol{r}) \, d^3r + G[n]. \tag{80}$$

This functional was first discussed by Foulkes and Haydock [12] and is sometimes called the generalized Harris or generalized Harris-Foulkes functional [8]. The one-electron eigenvalues $\epsilon_i[V_{\text{eff}}]$ are obtained by solving

$$\left(-\frac{1}{2}\nabla^2 + V_{\text{eff}}(\boldsymbol{r}) \right) \psi_i(\boldsymbol{r}) = \epsilon_i[V_{\text{eff}}] \, \psi_i(\boldsymbol{r}). \tag{81}$$

Note that the evaluation of $E_{\text{GHF}}[n, V_{\text{eff}}]$ for given inputs $n(\boldsymbol{r})$ and $V_{\text{eff}}(\boldsymbol{r})$ requires the one-electron Schrödinger equation to be solved once only; no self-consistent looping is required.

A further simplification is to set $V_{\text{eff}}(\boldsymbol{r})$ equal to $V_{\text{KS}}([n], \boldsymbol{r})$. Since $V_{\text{eff}}(\boldsymbol{r})$ and $V_{\text{KS}}([n], \boldsymbol{r})$ are the same in the ground state, this does not affect the location of the stationary point. The resulting functional of $n(\boldsymbol{r})$ only is called the Harris or Harris-Foulkes functional [25, 12, 8]:

$$E_{\text{HF}}[n] = \sum_{i \text{ occ}} \epsilon_i[n] - \int V_{\text{KS}}([n], \boldsymbol{r}) n(\boldsymbol{r}) \, d^3r + G[n]. \tag{82}$$

The energy eigenvalues $\epsilon_i[n]$ are now obtained by solving

$$\left(-\frac{1}{2}\nabla^2 + V_{\text{KS}}([n], \boldsymbol{r}) \right) \psi_i(\boldsymbol{r}) = \epsilon_i[n] \, \psi_i(\boldsymbol{r}). \tag{83}$$

As in the case of $E_{\text{GHF}}[n, V_{\text{eff}}]$, no-selfconsistent looping is required to evaluate $E_{\text{HF}}[n]$ for a given $n(\boldsymbol{r})$.

Both $E_{\text{GHF}}[n, V_{\text{eff}}]$ and $E_{\text{HF}}[n]$ are stationary about the ground state, a property that could in principle be used to guide an iterative, self-consistent algorithm towards the exact ground-state energy and density. In most cases, however, this has no advantages over the standard approach using the Hohenberg-Kohn-Sham functional. The main uses of $E_{\text{GHF}}[n, V_{\text{eff}}]$ and $E_{\text{HF}}[n]$ are in non-selfconsistent DFT calculations.

3.4   The tight-binding total energy method as a stationary approximation to density-functional theory

Let us return to the generalized Harris functional, Eq. (80), and the corresponding one-electron problem, Eq. (81). The functional is stationary about the exact ground state, so evaluating it for input densities and potentials close to the ground state produces total energies with second-order errors. With this in mind, we choose an input density in the form of a superposition of spherical densities,

$$n^{\text{in}}(\boldsymbol{r}) = \sum_I n_I(|\boldsymbol{r} - \boldsymbol{d}_I|), \tag{84}$$

and an input potential in the form of a superposition of spherical atomic-like potentials,

$$V_{\text{eff}}^{\text{in}}(\boldsymbol{r}) = \sum_I V_{\text{eff},I}(|\boldsymbol{r} - \boldsymbol{d}_I|). \tag{85}$$

For most solids, it is possible to construct superpositions of spherical atomic-like densities and potentials that match the exact ground-state density and Kohn-Sham potential rather well. The spherical densities required to describe a highly ionic solid might, of course, be ionic, integrating to produce a net atomic charge. Once the approximate potential and density have been constructed, we solve Eq. (81) non-selfconsistently to find the one-electron eigenvalues $\epsilon_i[V_{\text{eff}}^{\text{in}}]$. The energy functional $E_{\text{GHF}}[n^{\text{in}}, V_{\text{eff}}^{\text{in}}]$ is then evaluated using Eq. (80).

Because $V_{\text{eff}}^{\text{in}}(\boldsymbol{r})$ is a superposition of spherical atomic-like potentials, the one-electron Hamiltonian has exactly the form assumed in Sec. 2.2.4. We can therefore find the one-electron eigenvalues by choosing a basis set of atomic-like orbitals, constructing the one-, two- and three-center contributions to the tight-binding Hamiltonian and overlap matrices, and solving the generalized tight-binding eigenvalue problem. Furthermore, since both $V_{\text{eff}}^{\text{in}}$ and n^{in} are superpositions of spherical functions, almost all of the double-counting corrections appearing in Eq. (80) are strictly pairwise. The only exceptions are the exchange-correlation terms, which retain some weak non-pairwise character because $E_{\text{xc}}[n]$ is not a simple quadratic functional of n. In the exchange-only version of the local density approximation, for example, $E_{\text{xc}}[n]$ is proportional to the integral of $n^{4/3}(\boldsymbol{r})$ over the system.

If we ignore the small three- and higher-center contributions to the exchange-correlation double-counting terms, we have succeeded in deriving something very close to a tight-binding total energy model [11, 12]. The potential of the solid is approximated as a superposition of spherical atomic-like contributions, and the corresponding one-electron Schrödinger equation is solved once, non-selfconsistently, using a basis set of localized atomic-like functions. The total energy is the sum of the occupied eigenvalues and an (almost) pairwise ion-ion repulsion. The variational principle ensures that the calculated total energy decreases systematically towards $E[n^{\text{in}}, V_{\text{eff}}^{\text{in}}]$ as the basis set is improved; and the stationarity of the GHF functional ensures that $E[n^{\text{in}}, V_{\text{eff}}^{\text{in}}] - E_0$ is quadratic in $n^{\text{in}}(\boldsymbol{r}) - n_0(\boldsymbol{r})$ and $V_{\text{eff}}^{\text{in}}(\boldsymbol{r}) - V_{\text{KS}}([n_0], \boldsymbol{r})$.

The first derivation of the tight-binding total energy method [11, 12] from DFT was based on the Harris functional of the density only, with an input density in the form of a superposition of spherical atomic-like densities. The exchange-correlation contributions to the effective potential

$V_{\text{KS}}([n^{\text{in}}], \boldsymbol{r})$ appearing in Eq. (83) cannot then be written as a sum of spherical atomic-like contributions, which complicates the argument somewhat, but the conclusions are similar.

The accuracy of the Harris functional used with a superposition of spherical atomic-like densities has been tested for a wide range of solids [26–28] with surprising success. It is often capable of producing quantitatively accurate results, especially if the spherical atomic-like densities are optimized in some way [?, 28]. It does not work so well in transition metals, where the electronic configuration of an atom in the solid may be very different from that of an isolated atom, and often fails in ionic solids with significant charge transfer. In cases like these self-consistent tight-binding calculations are required [30–33].

4 Coulomb interactions for s, p, and d electrons

Although DFT is exact in principle, real DFT calculations require approximate exchange-correlation functionals. These are hard to improve systematically and do not always work as well as one might hope. Furthermore, the version of DFT described here yields ground-state properties only (time-dependent DFT [34] gives some excited-state properties). What can we do if the exchange-correlation functional proves inaccurate or we wish to calculate quantities DFT cannot provide? The most natural option is to return to the many-electron Schrödinger equation, Eq. (39), and attempt to solve that directly. Are there tight-binding-like models for many-particle problems?

4.1 The tight-binding full-configuration-interaction method

The main feature of the tight-binding approach is the choice of a basis of atomic-like orbitals, $\phi_\alpha(\boldsymbol{r})$, with $\alpha = 1, 2, \ldots, M$. The many-electron wavefunction $\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)$, which is a totally antisymmetric function of N different electron positions, can be approximated as a linear combination of Slater determinants of these orbitals:

$$D_{\boldsymbol{\alpha}}(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_{\alpha_1}(\boldsymbol{r}_1) & \phi_{\alpha_2}(\boldsymbol{r}_1) & \ldots & \ldots & \phi_{\alpha_N}(\boldsymbol{r}_1) \\ \phi_{\alpha_1}(\boldsymbol{r}_2) & \phi_{\alpha_2}(\boldsymbol{r}_2) & \ldots & \ldots & \phi_{\alpha_N}(\boldsymbol{r}_2) \\ & & & & \\ & & & & \\ \phi_{\alpha_1}(\boldsymbol{r}_N) & \phi_{\alpha_2}(\boldsymbol{r}_N) & \ldots & \ldots & \phi_{\alpha_N}(\boldsymbol{r}_N) \end{vmatrix}, \qquad (86)$$

where $\boldsymbol{\alpha} = (\alpha_1, \alpha_2, \ldots, \alpha_N)$ lists the indices of the orbitals appearing in $D_{\boldsymbol{\alpha}}$. A Slater determinant containing the same orbital twice vanishes because it has two identical columns, so we can assume that all of the indices are different. The order in which the indices appear affects the sign of the determinant only, so it is often convenient to insist that $\alpha_1 < \alpha_2 < \ldots < \alpha_N$. Given a determinant for which this is not the case, one can always permute the indices into ascending order. Every pair interchange swaps two columns and changes the sign of the determinant, but nothing else is affected. We assume from now on that the one-electron basis set is

orthonormal, $\langle \phi_\alpha | \phi_\beta \rangle = \delta_{\alpha\beta}$, in which case the N-electron basis set of Slater determinants is also orthonormal:

$$\langle D_{\boldsymbol{\alpha}} | D_{\boldsymbol{\beta}} \rangle = \int D_{\boldsymbol{\alpha}}^*(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N) D_{\boldsymbol{\beta}}(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N) \, d^3r_1 d^3r_2 \ldots d^3r_N = \delta_{\boldsymbol{\alpha}\boldsymbol{\beta}}, \qquad (87)$$

where $\delta_{\boldsymbol{\alpha}\boldsymbol{\beta}} = \delta_{\alpha_1\beta_1}\delta_{\alpha_2\beta_2}\ldots\delta_{\alpha_N\beta_N}$ and the lists $(\alpha_1, \alpha_2, \ldots, \alpha_N)$ and $(\beta_1, \beta_2, \ldots, \beta_N)$ are in ascending order.

Because the one-electron basis set is finite, the N-electron basis of Slater determinants is far from complete. It is, however, huge. Consider, for example, a system of $N = 10$ electrons described using a basis set of $M = 20$ one-electron orbitals. The number of possible Slater determinants is the number of ways of picking N orbitals from a set of M possibilities. This is $^M C_N = {}^{20}C_{10} = 184,756$.

The next step is to approximate the eigenstates of the many-electron Hamiltonian as linear combinations of Slater determinants,

$$\Psi = \sum_{\boldsymbol{\alpha}} c_{\boldsymbol{\alpha}} D_{\boldsymbol{\alpha}}, \qquad (88)$$

and determine the optimal expansion coefficients using the linear variational method described in Sec. 2.1. The resulting matrix eigenvalue problem takes the form

$$\sum_{\boldsymbol{\beta}} H_{\boldsymbol{\alpha}\boldsymbol{\beta}} c_{\boldsymbol{\beta}} = E c_{\boldsymbol{\alpha}}, \qquad (89)$$

where $H_{\boldsymbol{\alpha}\boldsymbol{\beta}} = \langle D_{\boldsymbol{\alpha}} | \hat{H} | D_{\boldsymbol{\beta}} \rangle$. Note that $\hat{H}$ is the full N-electron Hamiltonian operator and $H_{\boldsymbol{\alpha}\boldsymbol{\beta}} = \langle D_{\boldsymbol{\alpha}} | \hat{H} | D_{\boldsymbol{\beta}} \rangle$ is a $3N$-dimensional integral. Fortunately, because $\hat{H}$ only contains one- and two-electron operators, all non-zero Hamiltonian matrix elements can be expressed in terms of three- and six-dimensional integrals. Solving the eigenvalue problem in Eq. (89) yields $^M C_N$ approximate eigenvalues and eigenfunctions of the exact many-electron Hamiltonian. These may also be viewed as exact eigenvalues and eigenfunctions of the projected Hamiltonian $\hat{P}\hat{H}\hat{P}$, where $\hat{P}$ is the projector onto the space spanned by the $^M C_N$ Slater determinants in the basis.

This approach is very difficult to use because of the enormous size of the many-electron Hilbert space, but is useful for small atoms and molecules. Chemists call it the full configuration interaction method. Seen from the point of view of this article, it is the many-electron equivalent of the tight-binding method.

4.1.1 Second-quantized notation

The projected Hamiltonian $\hat{P}\hat{H}\hat{P}$ corresponding to the real-space Hamiltonian

$$\hat{H} = \sum_i \left(-\frac{1}{2}\nabla_i^2 + V_{\text{nuc}}(\boldsymbol{r}_i) \right) + \sum_{i>j} \frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} \qquad (90)$$

may be written in second-quantized notation as

$$\hat{H} = \sum_{\alpha,\beta} h_{\alpha\beta} \, \hat{c}_\alpha^\dagger \hat{c}_\beta + \frac{1}{2} \sum_{\alpha,\beta,\chi,\gamma} V_{\alpha\beta,\chi\gamma} \, \hat{c}_\alpha^\dagger \hat{c}_\beta^\dagger \hat{c}_\gamma \hat{c}_\chi, \qquad (91)$$

where $\hat{c}_\alpha^\dagger$ and $\hat{c}_\alpha$ are creation and annihilation operators for electrons in the one-electron orbital $\phi_\alpha(\boldsymbol{r})$ and

$$h_{\alpha\beta} = \int \phi_\alpha^*(\boldsymbol{r}) \left(-\frac{1}{2}\nabla_i^2 + V_{\text{nuc}}(\boldsymbol{r}) \right) \phi_\beta(\boldsymbol{r})\, d^3r, \tag{92}$$

$$V_{\alpha\beta,\chi\gamma} = \iint \phi_\alpha^*(\boldsymbol{r})\phi_\beta^*(\boldsymbol{r}') \frac{1}{|\boldsymbol{r} - \boldsymbol{r}'|} \phi_\chi(\boldsymbol{r})\phi_\gamma(\boldsymbol{r}')\, d^3r d^3r', \tag{93}$$

are the one- and two-particle Hamiltonian matrix elements. The creation and annihilation operators satisfy the anticommutation relations:

$$\left\{ \hat{c}_\alpha, \hat{c}_\beta^\dagger \right\} = \hat{c}_\alpha\hat{c}_\beta^\dagger + \hat{c}_\beta^\dagger\hat{c}_\alpha = \delta_{\alpha\beta}. \tag{94}$$

Second-quantized notation is explained in the first chapter of almost every book on many-body theory; the dense but precise explanation given by Negele and Orland [35] is a good one. It is important to understand that "second quantization" is a misnomer: the second-quantized notation brings nothing new except algebraic convenience; the second-quantized Hamiltonian is exactly the same as the original N-electron Hamiltonian; and the basis set of Slater determinants has not changed.

The systems for which DFT fails and many-body tight-binding methods are most useful are often magnetic, so we can no longer ignore the electron spin. The spin-dependent tight-binding basis functions take the form

$$\phi_{\alpha,\zeta}(\boldsymbol{r}, s) = \phi_\alpha(\boldsymbol{r})\chi_\zeta(s), \tag{95}$$

where $s = \uparrow, \downarrow$ and χ_ζ is either $\chi_\uparrow$ or $\chi_\downarrow$, with $\chi_\uparrow(s) = \delta_{s,\uparrow}$ and $\chi_\downarrow(s) = \delta_{s,\downarrow}$. Note that the spatial parts of the basis functions are independent of spin; this is by choice. The spin-dependent Hamiltonian is

$$\hat{H} = \sum_\zeta \sum_{\alpha,\beta} h_{\alpha\beta}\, \hat{c}_{\alpha,\zeta}^\dagger \hat{c}_{\beta,\zeta} + \frac{1}{2} \sum_{\zeta,\zeta'} \sum_{\alpha,\beta,\chi,\gamma} V_{\alpha\beta,\chi\gamma}\, \hat{c}_{\alpha,\zeta}^\dagger \hat{c}_{\beta,\zeta'}^\dagger \hat{c}_{\gamma,\zeta'}\hat{c}_{\chi,\zeta}, \tag{96}$$

where $\hat{c}_{\alpha,\zeta}^\dagger$ and $\hat{c}_{\alpha,\zeta}$ are the creation and annihilation operators for the basis function $\phi_{\alpha,\zeta}(\boldsymbol{r}, s)$ and satisfy the commutation relations

$$\left\{ \hat{c}_{\alpha,\zeta}, \hat{c}_{\beta,\zeta'}^\dagger \right\} = \delta_{\alpha\beta}\delta_{\zeta\zeta'}. \tag{97}$$

Because the spatial parts of the basis functions were chosen to be independent of spin, the matrix elements $h_{\alpha\beta}$ and $V_{\alpha\beta,\chi\gamma}$ are still as given in Eqs. (92) and (93). Relativistic spin-dependent interactions such as the spin-orbit term have not been included but can easily be added.

The Hamiltonian as expressed in Eq. (96) is closely related to the tight-binding Hamiltonian considered earlier. The one-electron matrix elements $h_{\alpha\beta}$ are analogous to the tight-binding matrix elements $H_{\alpha\beta} = \langle\phi_\alpha|(-\frac{1}{2}\nabla^2 + V_{\text{eff}}(\boldsymbol{r})|\phi_\beta\rangle$, except that the nuclear potential appears in place of the effective potential. These matrix elements can be parametrized in terms of a small number of Slater-Koster parameters, just as in tight-binding theory. The two-particle Coulomb interaction matrix elements $V_{\alpha\beta,\chi\gamma}$ are more complicated. In DFT-based tight-binding

methods they are replaced by the density-dependent Hartree and exchange-correlation potentials incorporated into V_{eff}.

Switching to a second-quantized formalism has improved the notation but has not made the many-electron problem any easier to solve. The complicated form of Eq. (91) is also an impediment to pencil-and-paper work. Even if we consider only the three p orbitals on a single atom, the interaction matrix $V_{\alpha\beta,\chi\gamma}$ has $3^4 = 81$ elements. For the five d orbitals this rises to $5^4 = 625$ elements. Such large collections of numbers are not easy to deal with analytically, so simplifications are required.

The first simplification, often made in the many-body community, is to neglect all Coulomb integrals involving orbitals on more than one atom. Given the long range of the Coulomb interaction this seems unintuitive at first, and quantum chemists, who like to get things *right*, normally prefer to evaluate all of the matrix elements for all of the orbitals. Most of the many-body problems studied by condensed matter physicists, however, concern atoms in solids, often metals, where the interactions between atoms are strongly screened by mobile valence electrons. In many cases this screening is so efficient that electrons occupying localized d of f orbitals on one atom interact only weakly with electrons in d or f orbitals on other atoms and the screened inter-atomic Coulomb matrix elements really can be ignored. The mobile valence electrons are not included in the tight-binding model explicitly, but their effect is to renormalize the matrix elements between the localized orbitals that are included.

4.1.2 Coulomb interactions on a single atom

The rest of this article discusses what we know about the symmetries of the matrix $V_{\alpha\beta,\chi\gamma}$ that describes the (screened) Coulomb interactions on a single atom. Can we carry out an equivalent of the Slater-Koster analysis, allowing us to express the elements of $V_{\alpha\beta,\chi\gamma}$ in terms of a minimal set of basic parameters? How many parameters do we need?

These are questions with a long history, but they still cause a great deal of confusion. The forms of $V_{\alpha\beta,\chi\gamma}$ for shells of s and p electrons are well established, but many different d-shell Hamiltonians have been proposed and most of them are wrong in one way or another. Some are missing essential symmetries, failing to remain invariant under rotations in real and/or spin space; others are missing terms no smaller than the terms kept; and even the best are missing terms thought to be small. Many otherwise sophisticated papers on many-body physics start with an incorrect model Hamiltonian and may reach false conclusions as a result. The history of the subject and the failings of some of the most widely used Hamiltonians are summarized in Ref. [13], which also clears up the confusion for shells of s, p and d electrons. Here we explain the results derived in that paper.

Before going on, we remark that the correct form of the on-site Coulomb operator has been known for more than 50 years and that quantum chemists use it as a matter of course. If we assume that the $2l + 1$ basis functions in a shell of angular momentum l have the same angular dependence as the spherical harmonics Y_l^m, with $m = -l, -l+1, \ldots, l$, the theory of angular momentum [36] may be used to derive formulae for $V_{\alpha\beta,\chi\gamma}$. See Ref. [37] for a clear explanation.

The drawback of this approach is that the formulae are complicated and expressed in terms of quantities such as Gaunt or Racah coefficients, which are inconvenient for analytic work. The formulae derived here are less general, in that they apply to s, p and d shells only, but simpler. The most important symmetry of $V_{\alpha\beta,\chi\gamma}$ is rotational invariance. If the basis functions used to describe a shell of angular momentum l have the same angular dependence as spherical harmonics Y_l^m, the orbital label α may be identified with the m index. Such basis functions transform into linear combinations of each other under rotations:

$$\hat{R}^{\boldsymbol{\omega}}\phi_\alpha = \sum_{\alpha'=-l}^{l} D_{\alpha',\alpha}^l(\boldsymbol{\omega})\phi_{\alpha'}. \tag{98}$$

The operator $\hat{R}^{\boldsymbol{\omega}}$ rotates the function to which it is applied by ω radians about an axis parallel to the unit vector $\hat{\boldsymbol{\omega}}$, and $D^l(\boldsymbol{\omega})$ is the $(2l+1) \times (2l+1)$ matrix corresponding to $\hat{R}^{\boldsymbol{\omega}}$ in the irreducible representation of the rotation group of angular momentum l. The Coulomb interaction $1/|\boldsymbol{r}-\boldsymbol{r}'|$ is unchanged if $\boldsymbol{r}$ and $\boldsymbol{r}'$ are rotated simultaneously, so $V_{\alpha\beta,\chi\gamma}$ does not change if every orbital is replaced by a rotated version:

$$\begin{aligned}
V_{\alpha\beta,\chi\gamma} &= \iint \phi_\alpha^*(\boldsymbol{r})\phi_\beta^*(\boldsymbol{r}') \frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|} \phi_\chi(\boldsymbol{r})\phi_\gamma(\boldsymbol{r}')\, d^3r\, d^3r' \\
&= \iint \left(\hat{R}^{\boldsymbol{\omega}}\phi_\alpha(\boldsymbol{r})\right)^* \left(\hat{R}^{\boldsymbol{\omega}}\phi_\beta(\boldsymbol{r}')\right)^* \frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|} \left(\hat{R}^{\boldsymbol{\omega}}\phi_\chi(\boldsymbol{r})\right) \left(\hat{R}^{\boldsymbol{\omega}}\phi_\gamma(\boldsymbol{r}')\right)\, d^3r\, d^3r' \\
&= \sum_{\alpha'\beta'\chi'\gamma'} \left(D_{\alpha',\alpha}^l(\boldsymbol{\omega})\right)^* \left(D_{\beta',\beta}^l(\boldsymbol{\omega})\right)^* V_{\alpha'\beta',\chi'\gamma'} D_{\chi',\chi}^l(\boldsymbol{\omega}) D_{\gamma',\gamma}^l(\boldsymbol{\omega}). \tag{99}
\end{aligned}$$

This shows that $V_{\alpha\beta,\chi\gamma}$ is a rotationally invariant fourth-rank tensor. If the basis functions are defined using the real spherical harmonics $\tilde{Y}_m^l$ introduced in Sec. 2.2.5, the D^l matrices, which are complex and unitary, are replaced by the $\tilde{D}^l$ matrices from Eq. (18), which are real and orthogonal. Since most Hubbard-like models use real spherical harmonics, we are primarily interested in this case.

4.2 Hubbard-like Hamiltonians for atoms

4.2.1 The one-band Hubbard model: s-orbital symmetry

If the outermost shell is an s shell and all other shells are ignored, the model Hamiltonian for an atom has only one spatial orbital ϕ_α and one non-zero Coulomb matrix element $V_{\alpha\alpha,\alpha\alpha}$, which is called the Hubbard parameter and denoted U_0. The interaction Hamiltonian takes the form

$$\hat{V} = \frac{1}{2}U_0 \sum_{\zeta,\zeta'} \hat{c}_{\alpha,\zeta}^\dagger \hat{c}_{\alpha,\zeta'}^\dagger \hat{c}_{\alpha,\zeta'} \hat{c}_{\alpha,\zeta} = \frac{1}{2}U_0 \left(\hat{c}_{\alpha,\uparrow}^\dagger \hat{c}_{\alpha,\downarrow}^\dagger \hat{c}_{\alpha,\downarrow} \hat{c}_{\alpha,\uparrow} + \hat{c}_{\alpha,\downarrow}^\dagger \hat{c}_{\alpha,\uparrow}^\dagger \hat{c}_{\alpha,\uparrow} \hat{c}_{\alpha,\downarrow} \right) = U_0\, \hat{n}_{\alpha,\uparrow} \hat{n}_{\alpha,\downarrow}, \tag{100}$$

where I have noted that $\hat{c}_{\alpha,\zeta} \hat{c}_{\alpha,\zeta} = 0$, reordered the creation and annihilation operators using the anticommutation relations, and introduced the number operator $\hat{n}_{\alpha,\zeta} = \hat{c}_{\alpha,\zeta}^\dagger \hat{c}_{\alpha,\zeta}$, which counts

how many electrons are in basis state $\phi_{\alpha,\zeta}$. Equation (100) is the famous Hubbard interaction and is the starting point for much of the analytic work on strongly interacting systems.

It is often convenient to rewrite the atomic interaction Hamiltonian in terms of the operators for the total number of electrons on the atom,

$$\hat{n} = \sum_{\alpha,\zeta} \hat{n}_{\alpha,\zeta}, \tag{101}$$

and the electronic spin moment of the atom,

$$\hat{\boldsymbol{m}} = \sum_{\alpha,\zeta,\zeta'} \hat{c}^{\dagger}_{\alpha,\zeta} \boldsymbol{\sigma}_{\zeta,\zeta'} \hat{c}_{\alpha,\zeta'}, \tag{102}$$

where $\boldsymbol{\sigma}_{\zeta,\zeta'} = (\sigma^x_{\zeta,\zeta'}, \sigma^y_{\zeta,\zeta'}, \sigma^z_{\zeta,\zeta'})$ is the vector of Paul spin matrices

$$\sigma^x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \qquad \sigma^y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \text{and} \quad \sigma^z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

In the case of an s shell there is only one spatial orbital and the sums over α in Eqs. (101) and (102) have only one term each.

The square of the number operator for an s shell is

$$\hat{n}^2 = (\hat{n}_{\alpha,\uparrow} + \hat{n}_{\alpha,\downarrow})(\hat{n}_{\alpha,\uparrow} + \hat{n}_{\alpha,\downarrow}) = 2\hat{n}_{\alpha,\uparrow}\hat{n}_{\alpha,\downarrow} + \hat{n}_{\alpha,\uparrow} + \hat{n}_{\alpha,\downarrow} = 2\hat{n}_{\alpha,\uparrow}\hat{n}_{\alpha,\downarrow} + \hat{n}, \tag{103}$$

where we have noted that $\hat{n}_{\alpha,\sigma}\hat{n}_{\alpha,\sigma} = \hat{n}_{\alpha,\sigma}$. The Hubbard interaction for an s shell may therefore be rewritten in terms of the operator for the total number of electrons as

$$\hat{V} = \frac{1}{2}U_0 \left(\hat{n}^2 - \hat{n}\right). \tag{104}$$

The one-electron $-\hat{n}$ term on the right-hand side of Eq. (103) arises because the creation operators in $\hat{n}^2$ are not all to the left of the annihilation operators; if we attempt to reorder the creation and annihilation operators to ensure that this is the case, the anticommutators produce additional one-electron terms. This mixing of one- and two-electron terms is awkward, so we define $:\hat{n}^2:$, the "normal ordered" version of $\hat{n}^2$, by permuting the creation and annihilation operators until all of the creation operators are on the left, *without* adding the anticommutator terms that would be required to leave the product of operators unaltered. If the rearrangement requires an odd number of flips, the normal ordering also introduces a sign change. It is easy to show quite generally (not just for an s shell) that

$$:\hat{n}^2: \; = \hat{n}^2 - \hat{n}, \tag{105}$$

so we can write the s-shell Hubbard interaction as

$$\hat{V} = \frac{1}{2}U_0 :\hat{n}^2: . \tag{106}$$

The s-band Hubbard interaction can also be written in terms of $:\hat{m}^2:\ =\ :\boldsymbol{\hat{m}}\cdot\boldsymbol{\hat{m}}:$. Using the identity $\boldsymbol{\sigma}_{\zeta\zeta'}\cdot\boldsymbol{\sigma}_{\xi\xi'}=2\delta_{\zeta'\xi}\delta_{\zeta\xi'}-\delta_{\zeta\zeta'}\delta_{\xi\xi'}$, one finds that

$$:\hat{m}^2:\ =\ -\sum_{\alpha\beta}\sum_{\zeta\xi}\left(2\hat{c}^\dagger_{\alpha,\zeta}\hat{c}^\dagger_{\beta,\xi}\hat{c}_{\alpha,\xi}\hat{c}_{\beta,\zeta}+\hat{c}^\dagger_{\alpha,\zeta}\hat{c}^\dagger_{\beta,\xi}\hat{c}_{\beta,\xi}\hat{c}_{\alpha,\zeta}\right)=\hat{m}^2-3\hat{n}. \tag{107}$$

For an s shell this is equivalent to

$$:\hat{m}^2:\ =\ -6\hat{n}_{\alpha,\uparrow}\hat{n}_{\alpha,\downarrow}=-3:\hat{n}^2: \tag{108}$$

and we obtain

$$\hat{V}=-\frac{1}{6}U_0:\hat{m}^2:\ . \tag{109}$$

4.2.2   The three-band Hubbard model: p-orbital symmetry

Suppose that the orbitals α, β, χ, and γ are real spherical harmonic p orbitals with angular dependence x/r, y/r and z/r. The rotation matrix $D^l_{\alpha'\alpha}(\boldsymbol{\omega})$ is then a familiar Cartesian 3×3 rotation matrix $\boldsymbol{R}_{\boldsymbol{\omega}}$, and $V_{\alpha\beta,\chi\gamma}$ is a rotationally invariant fourth-rank Cartesian tensor. The general form of such a tensor is well known [38]:

$$V_{\alpha\beta,\chi\gamma}=U\delta_{\alpha\chi}\delta_{\beta\gamma}+J\delta_{\alpha\gamma}\delta_{\beta\chi}+J'\delta_{\alpha\beta}\delta_{\chi\gamma}, \tag{110}$$

where $U=V_{\alpha\beta,\alpha\beta}$, $J=V_{\alpha\beta,\beta\alpha}$, and $J'=V_{\alpha\alpha,\beta\beta}$, all with $\alpha\neq\beta$.

Bearing in mind that the Cartesian p orbitals are real, a brief inspection of the form of the matrix element, Eq. (93), shows that $V_{\alpha\beta,\chi\gamma}=V_{\chi\beta,\alpha\gamma}=V_{\alpha\gamma,\chi\beta}$, implying that $J=J'$. Hence we find

$$V_{\alpha\beta,\chi\gamma}=U\delta_{\alpha\chi}\delta_{\beta\gamma}+J(\delta_{\alpha\gamma}\delta_{\beta\chi}+\delta_{\alpha\beta}\delta_{\chi\gamma}). \tag{111}$$

This shows that the most general p-shell on-site Coulomb interaction Hamiltonian is defined by just two independent parameters; the interaction matrix $V_{\alpha\beta,\chi\gamma}$ still has 81 elements, but only two are independent. Setting $\alpha=\beta=\chi=\gamma$ recovers the well-known equation $U_0=U+2J$, where $U_0=V_{\alpha\alpha,\alpha\alpha}$.

Starting from Eq. (111) and wading through lots of algebra, it is straightforward but tedious to show that the Coulomb interaction Hamiltonian may be written:

$$\hat{V}=\frac{1}{2}\left[(U-J):\hat{n}^2:\ -J:\hat{m}^2:\ -J:\hat{L}^2:\ \right], \tag{112}$$

where

$$\boldsymbol{\hat{L}}=i\sum_{\alpha\beta\zeta}\left(\epsilon_{1\beta\alpha},\epsilon_{2\beta\alpha},\epsilon_{3\beta\alpha}\right)\hat{c}^\dagger_{\alpha,\zeta}\hat{c}_{\beta,\zeta} \tag{113}$$

is the vector angular momentum operator, $\epsilon_{\alpha\beta\gamma}$ is the three-dimensional Levi-Civita symbol, and $\hat{L}^2=\boldsymbol{\hat{L}}\cdot\boldsymbol{\hat{L}}$. An equivalent expression is

$$\hat{V}=\frac{1}{2}\left[\left(U-\frac{1}{2}J\right):\hat{n}^2:\ -\frac{1}{2}J:\hat{m}^2:\ +J\sum_{\alpha\beta}:(\hat{n}_{\alpha\beta})^2:\ \right], \tag{114}$$

where the operator $\hat{n}_{\alpha\beta} = \sum_\zeta \hat{c}^\dagger_{\alpha,\zeta} \hat{c}_{\beta,\zeta}$ transfers an electron of either spin from orbital β to orbital α. The normal-ordered square of this operator,

$$: (\hat{n}_{\alpha\beta})^2: \ = \sum_{\zeta,\zeta'} : \hat{c}^\dagger_{\alpha,\zeta} \hat{c}_{\beta,\zeta} \hat{c}^\dagger_{\alpha,\zeta'} \hat{c}_{\beta,\zeta'}: \ = 2 \left(\hat{c}_{\alpha,\uparrow} \hat{c}_{\alpha,\downarrow} \right)^\dagger \left(\hat{c}_{\beta,\uparrow} \hat{c}_{\beta,\downarrow} \right), \tag{115}$$

describes the hopping of singlet pairs of electrons from spatial orbital β to spatial orbital α. Equation (112) exemplifies Hund's first and second rules for the atom. Noting that $\hat{\boldsymbol{m}} = 2\hat{\boldsymbol{S}}$, where $\hat{\boldsymbol{S}}$ is the electron spin operator, we see that the energy is minimized by first maximizing the spin (prefactor $-2J$) and then maximizing the orbital angular momentum (prefactor $-\frac{1}{2}J$).

4.2.3 The five-band Hubbard model: d-orbital symmetry

If we consider Eq. (99) for a shell of d orbitals, the matrices D^l belong to the five-dimensional $l = 2$ irreducible representation of the rotation group; they are no longer the familiar 3×3 Cartesian rotation matrices. One way to determine the number of independent parameters required to specify $V_{\alpha\beta,\chi\gamma}$ completely is to use the theory of angular momentum [36], but we find it easier to use the theory of irreducible Cartesian tensors [39]. This allows us to re-express the behavior of $V_{\alpha\beta,\chi\gamma}$ under rotations using 3×3 rotation matrices only.

A Cartesian tensor of rank n transforms under rotation in the standard way:

$$(\hat{R}^{\boldsymbol{\omega}} T)_{ij\ldots k} = \sum_{i'j'\ldots k'} R^{\boldsymbol{\omega}}_{ii'} R^{\boldsymbol{\omega}}_{jj'} \ldots R^{\boldsymbol{\omega}}_{kk'} T_{i'j'\ldots k'}, \tag{116}$$

with $R^{\boldsymbol{\omega}}$ the 3×3 matrix for a rotation of ω radians about an axis parallel to $\hat{\boldsymbol{\omega}}$. This mapping transforms the 3^n elements of T into linear combinations of each other, so the elements form a basis for a 3^n-dimensional representation of the rotation group. In general, however, this representation is reducible. An *irreducible* Cartesian tensor of rank n and angular momentum l transforms in the same way as a general Cartesian tensor, but only has $2l + 1$ independent components. The rule for rotating the tensor, Eq. (116), transforms these $2l + 1$ independent components into linear combinations of each other, so they form a basis for a $2l + 1$ dimensional representation of the rotation group. The Cartesian tensor is said to be irreducible if this representation is irreducible.

We can illustrate these ideas by considering the tensor product of two vectors:

$$T = \boldsymbol{a} \otimes \boldsymbol{b} = \begin{pmatrix} a_1 b_1 & a_1 b_2 & a_1 b_3 \\ a_2 b_1 & a_2 b_2 & a_2 b_3 \\ a_3 b_1 & a_3 b_2 & a_3 b_3 \end{pmatrix}. \tag{117}$$

The nine elements of this tensor transform into linear combinations of each other under rotations, so they are a basis for a nine-dimensional representation of the rotation group. If we wanted to, we could construct the 9×9 matrix corresponding to the action of any given rotation directly from the tensorial transformation rule. We would find, however, that the 9×9 representation is not irreducible. In fact, as we already know from the theory of the addition of angular momentum,

$$1 \otimes 1 = 0 \oplus 1 \oplus 2. \tag{118}$$

This implies that it must be possible to create from the set of nine independent elements a single rotationally invariant s function, a set of three p functions, and a set of five d functions. We can accomplish this explicitly by writing $\boldsymbol{a} \otimes \boldsymbol{b}$ as the sum of three tensors:

$$T_{ij} = (\boldsymbol{a} \otimes \boldsymbol{b})_{ij} = \frac{1}{3}(a_k b_k)\delta_{ij} + T_{\{ij\}} + \left[T_{(ij)} - \frac{1}{3}(a_k b_k)\delta_{ij}\right] \qquad (119)$$

where $T_{(ij)} \equiv \frac{1}{2}(T_{ij} + T_{ji})$, $T_{\{ij\}} \equiv \frac{1}{2}(T_{ij} - T_{ji})$, and the summation convention is in force for repeated suffices. The first term is a multiple of the unit tensor and hence transforms like an s function; the three non-zero independent elements of the antisymmetric tensor $T_{\{ij\}}$ are the components of the vector product $\boldsymbol{a} \times \boldsymbol{b}$ and transform under rotations like the three p functions; and the five independent elements of the traceless symmetric tensor $T_{(ij)} - \frac{1}{2}(a_k b_k)\delta_{ij}$ transform under rotations like the five Cartesian d orbitals. Note that antisymmetric matrices remain antisymmetric and traceless symmetric matrices remain traceless symmetric matrices when rotated.

If we choose $\boldsymbol{a} = \boldsymbol{b} = \boldsymbol{r} = (x, y, z)$, the d-like nature of the traceless symmetric part of $\boldsymbol{a} \otimes \boldsymbol{b}$ becomes obvious:

$$(\boldsymbol{r} \otimes \boldsymbol{r})_{(ij)} - \frac{1}{3}r^2 \delta_{ij} = \begin{pmatrix} x^2 - \frac{1}{3}r^2 & xy & xz \\ xy & y^2 - \frac{1}{3}r^2 & yz \\ xz & yz & z^2 - \frac{1}{3}r^2 \end{pmatrix}. \qquad (120)$$

The off-diagonal elements xy, yz and zx are the three t_{2g} functions; and the two independent diagonal elements, which we can take to be $3z^2 - r^2$ and $x^2 - y^2$, are the two e_g functions. We call this traceless symmetric tensor B from now on:

$$B_{ij} = (\boldsymbol{r} \otimes \boldsymbol{r})_{(ij)} - \frac{1}{3}r^2 \delta_{ij}. \qquad (121)$$

The link between the traceless symmetric tensor B and the d orbitals is a special case of a general result, which states that the $2l + 1$ independent elements of a totally symmetric l^{th} rank Cartesian tensor with all traces removed are a basis for the angular momentum l representation of the rotation group.

If we view every d orbital as an element (or linear combination of elements) of B, each d orbital may be labelled using two Cartesian indices i and j. The isotropic fourth-rank five-dimensional tensor $V_{\alpha\beta,\chi\gamma}$ from Eq. (93) then becomes an isotropic eighth-rank three-dimensional tensor $V_{ij,kl,mn,op}$, which transforms like $B_{ij}B_{kl}B_{mn}B_{op}$.

It is a theorem due to Weyl [40] that any isotropic Cartesian tensor of even rank can be expressed as a linear combination of products of Kronecker deltas, so the remaining task is to determine the number of independent products of four Kronecker deltas consistent with the symmetries of the eighth-rank tensor, bearing in mind that the second-rank tensors B of which it is composed are traceless and symmetric. The details of this calculation are explained in Ref. [13].

The result, translated back into the notation where each of the five d orbitals is labelled by a

single index with five possible values, is

$$V_{\alpha\beta,\chi\gamma} = \frac{1}{2}\left(U\delta_{\alpha\chi}\delta_{\beta\gamma} + \left[J + \frac{5}{2}\Delta J\right](\delta_{\alpha\gamma}\delta_{\beta\chi} + \delta_{\alpha\beta}\delta_{\gamma\chi}) - 48\Delta J\sum_{ijkl}\xi_{\alpha ij}\xi_{\beta jk}\xi_{\chi kl}\xi_{\gamma li}\right),$$

(122)

where $\boldsymbol{\xi}$ is a five-component vector of the traceless symmetric 3×3 transformation matrices used to convert from the two-index notation to the one-index notation:

$$\xi_1 = \begin{pmatrix} -\frac{1}{2\sqrt{3}} & 0 & 0 \\ 0 & -\frac{1}{2\sqrt{3}} & 0 \\ 0 & 0 & \frac{1}{\sqrt{3}} \end{pmatrix}, \xi_2 = \begin{pmatrix} 0 & 0 & \frac{1}{2} \\ 0 & 0 & 0 \\ \frac{1}{2} & 0 & 0 \end{pmatrix}, \xi_3 = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & \frac{1}{2} \\ 0 & \frac{1}{2} & 0 \end{pmatrix}, \xi_4 = \begin{pmatrix} 0 & \frac{1}{2} & 0 \\ \frac{1}{2} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \xi_5 = \begin{pmatrix} \frac{1}{2} & 0 & 0 \\ 0 & -\frac{1}{2} & 0 \\ 0 & 0 & 0 \end{pmatrix}.$$

The indices $(1, 2, 3, 4, 5)$ correspond to the d orbitals $(3z^2 - r^2, zx, yz, xy, x^2 - y^2)$. The three independent parameters U, J and ΔJ are defined as follows:

$$U = V_{(zx)(yz),(zx)(yz)},$$

(123)

$$J = \frac{1}{2}\left(V_{(zx)(yz),(yz)(zx)} + V_{(3z^2-r^2)(x^2-y^2),(x^2-y^2)(3z^2-r^2)}\right),$$

(124)

$$\Delta J = V_{(3z^2-r^2)(x^2-y^2),(x^2-y^2)(3z^2-r^2)} - V_{(zx)(yz),(yz)(zx)}.$$

(125)

U is the Hartree term between pairs of t_{2g} orbitals, J is the average of the e_g and t_{2g} exchange integrals, and ΔJ is the difference between the e_g and t_{2g} exchange integrals. These definitions are the same as those used by Oleś and Stollhoff [41], but our Hamiltonian, unlike theirs, is rotationally invariant in orbital space.

Rewriting Eq. (122) in terms of rotationally invariant operators gives

$$\hat{V} = \frac{1}{2}\left[(U - \frac{1}{2}J + 5\Delta J):\hat{n}^2: - \frac{1}{2}(J - 6\Delta J):\hat{m}^2: + (J - 6\Delta J)\sum_{\alpha\beta}:(\hat{n}_{\alpha\beta})^2: + \frac{2}{3}\Delta J:\hat{Q}^2:\right].$$

(126)

where $\hat{Q}^2 = \sum_{\mu\nu}\hat{Q}_{\mu\nu}\hat{Q}_{\nu\mu}$ is the square of the on-site quadrupole operator defined and discussed in Ref. [13]. The mean-field versions of the s, p, and d Hamiltonians may also be found in that paper.

4.2.4 Comparison with the Stoner Hamiltonian

The interaction part of the Stoner Hamiltonian for shells of p and d orbitals is usually defined as

$$\hat{V}_{\text{Stoner}} = \frac{1}{2}(U - \frac{1}{2}J):\hat{n}^2: - \frac{1}{4}J:\hat{m}_z^2:.$$

(127)

The $\hat{m}_z^2$ term breaks rotational symmetry in spin space, so this is a collinear Stoner Hamiltonian, appropriate only in cases when the ground state breaks the rotational spin symmetry and chooses a z axis. We can, however, restore the spin-rotation invariance by replacing $\hat{m}_z^2$ by $\hat{m}^2$. This produces the vector Stoner Hamiltonian,

$$\hat{V}_{\hat{m}^2\text{Stoner}} = \frac{1}{2}(U - \frac{1}{2}J):\hat{n}^2: - \frac{1}{4}J:\hat{m}^2:,$$

(128)
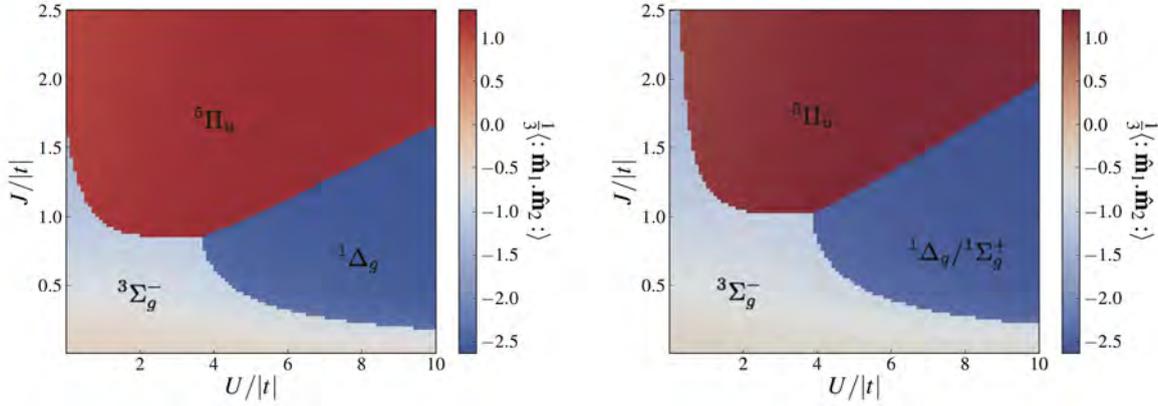
Fig. 10: *The magnetic correlation between two p-shell atoms, each with two electrons, as a function of the Hubbard parameters $U/|t|$ and $J/|t|$, where t is the $pp\sigma$ Slater-Koster parameter that describes the rate of electron hopping between atoms; the $pp\pi$ hopping parameter is $-t/2$. The regions of the graph are labelled by the symmetry of the ground state. The left-hand graph is generated using the full p-electron Hamiltonian from Sec. 4.2.2; the right-hand graph is generated using the vector Stoner Hamiltonian of Eq. (128). The Stoner phase diagram has a region with symmetry $^3\Sigma_g^-$ extending a long way up the J axis, which is not present when the full Hamiltonian is used. It also has a region with two degenerate ground states with symmetries $^1\Delta_g$ and $^1\Sigma_g^+$; this degeneracy is broken when the full p-electron Hamiltonian is used. From Ref. [13].*

which turns out to be identical to the Hamiltonian proposed by Dworin and Narath [42]. Working backwards from this Hamiltonian to the general form of the matrix element $V_{\alpha\beta,\chi\gamma}$ gives

$$V_{\alpha\beta,\chi\gamma}^{\hat{m}^2\text{Stoner}} = U\delta_{\alpha\chi}\delta_{\beta\gamma} + J\delta_{\alpha\gamma}\delta_{\beta\chi}, \tag{129}$$

which looks like the general p-shell result, Eq. (111), except that it is missing the $J\delta_{\alpha\beta}\delta_{\chi\gamma}$ term. Consequently, the vector Stoner Hamiltonian does not respect the invariance of the matrix element on interchange of α with χ or β with γ apparent from the form of Eq. (93) when the orbitals are real. As can be seen from Fig. 10, this omission affects the computed results significantly.

4.2.5 Conclusion

We have shown how to derive multi-band Hubbard-like Hamiltonians to describe shells of s, p, and d orbitals. There are important differences [13] between results obtained using the Hamiltonians derived here, which respect the symmetries of the problem, and the Stoner Hamiltonian, which does not. The vector version of the Stoner Hamiltonian misses the pair-hopping term present in our p- and d-shell Hamiltonians and the quadrupole term present in our d-shell Hamiltonian. The collinear version of the Stoner Hamiltonian breaks rotational symmetry in spin space, which makes it inappropriate for describing spin dynamics.

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