QUANTUM-MECHANICAL DESCRIPTION OF SOLIDS

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Summary

Although crystalline solids are composed of many interacting electrons and nuclei, many of their most important and useful properties may be described by single-electron quantum mechanics. Solids have discrete translational symmetry which means that there is an associated conserved quantity, the wavevector or crystal momentum. The single-electron energies are accordingly functions of the wavevector. The semi-classical equations of motion for an electron near a band extremeum show that derivatives of these energies with respect to the wavevector are related to the electron velocities and effective masses. Different methods have been developed for calculating the single-electron energies. Two of the most commonly employed are the pseudopotential method, which is based on extended states, and the tight-binding method, which is based on localized, atomic-like orbitals.

1. Introduction

1.1 The Many-Electron, Many-Ion Problem

Solids are composed of atoms of various types, held together by electrostatic interactions. Solids are characterized by greater or lesser degrees of order: most exhibit long-range order. Macroscopic examples of single crystals are more familiar than might first be imagined: diamonds and the thumbnail-sized silicon integrated circuits found in computers, audio and video equipment, automobiles and numerous other devices and appliances, for example. (Indeed, these silicon integrated circuits were in all likelihood cut from wafers which were originally part of a huge single silicon crystal 30 cm in diameter.) The interactions of the electrons and atomic nuclei in a given material determine its properties; the electrical characteristics (conducting, semi-conducting, or insulating) are most often employed in classifying substances. These properties are calculated using quantum mechanics, although the enormity of the problem -- there are of the order of 10^{22} atoms per cubic centimeter in many semiconductors -- would seem at first to render these calculations impossible. Actually, many of the most important properties of everyday materials are well-described by a single-electron (more properly, a single quasi-electron) picture, which treats all of the electrons in a solid as being independent and non-interacting, moving in a potential which incorporates both the electron-ion potential and an averaged interaction with all of the other electrons. This is commonly referred to as the self-consistent field approximation.

The reduction from many- to a single-particle quantum mechanics begins with an observation from atomic physics: changes in the configuration of the valence electrons do not significantly affect that of the core electrons. Thus the core orbitals are essentially fixed, regardless of the valence orbitals, and are unaltered in the variational calculation below. The full many-electron, many-ion Hamiltonian, ignoring relativistic effects, is:

$$\begin{aligned}\hat{H}_{tot} &\\ = \sum_{j=1}^{N}\frac{\mathbf{p}_j^2}{2m} + \frac{e^2}{8\pi\varepsilon_0}\sum_{i\neq j}^{N,N}\frac{1}{\left|\mathbf{r}_i-\mathbf{r}_j\right|} + \sum_{j=1}^{N'}\frac{\mathbf{P}_i^2}{2M_i} + \sum_{i\neq j}^{N',N'} V_{i-i}\left(\mathbf{R}_i-\mathbf{R}_j\right) &\\ + \sum_{i=1}^{N'}\sum_{j=1}^{N} V_{e-i}\left(\mathbf{r}_j-\mathbf{R}_i\right) &\end{aligned} \qquad (1)$$

where $\mathbf{p}_j$, $\mathbf{r}_j$ ($\mathbf{P}_i$, $\mathbf{R}_i$) are electron (ion) momenta and coordinates, respectively; and $V_{i\text{-}i}$ and $V_{e\text{-}i}$ are the ion-ion and electron-ion interactions, respectively. Equation (1) can be greatly simplified by taking advantage of the great disparity in the electron (m) and ion (M_i) masses. The fact that an ion is many thousands of times more massive than an electron suggests that the electrons might be treated in a first approximation by considering their motion in a fixed crystal (i.e., with all ions in their equilibrium positions), ignoring the ion motion which is expected to be rather insensitive to changes in the electron configuration. This results in separate electron- and ion-problems, the simplest approximation for the ion problem being that of quantum harmonic oscillators and leading to quantized lattice vibrations (phonons). Similarly, the ion coordinates appear as parameters in the electron problem: to lowest order the ions are assumed fixed at their equilibrium positions and electron and ion problems become decoupled. Since electron scattering by phonons is important, it is often desirable to consider the change in the electron-ion interaction potential from its equilibrium value to first order in the ion displacements. This is, however, easily treated for most cases of interest by perturbation theory applied to the solutions of the electron problem for the fixed crystal. Although limitations of space and scope preclude a rigorous justification of this separation, it is nevertheless clear that the starting point is the electron problem for the fixed crystal. The Hamiltonian for this system is:

$$\hat{H}_{tot} = \sum_{j=1}^{N} \frac{\mathbf{p}_j^2}{2m} + \frac{e^2}{8\pi\varepsilon_0} \sum_{i \neq j}^{N,N} \frac{1}{\left|\mathbf{r}_i - \mathbf{r}_j\right|} + \sum_{j=1}^{N} V\left(\mathbf{r}_j\right) \qquad V\left(\mathbf{r}_j\right) = \sum_{i=1}^{N'} V_{e-i}\left(\mathbf{r}_j - \mathbf{R}_i\right) \tag{2}$$

where the $\mathbf{R}_i$ are now the equilibrium ion positions.

Equation (2) is still formidable for it is a many-electron problem. Since electrons are fermions, the many-electron wavefunction must be anti-symmetric under the exchange of any two electrons (Pauli Exclusion Principle). This anti-symmetry is enforced by choosing as basis states Slater determinants:

$$\begin{aligned} &\Phi\left(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n; \eta_1, \eta_2, \ldots, \eta_N\right) \\ &= \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1\left(\mathbf{r}_1; \eta_1\right) & \cdots & \varphi_N\left(\mathbf{r}_1; \eta_1\right) \\ \vdots & \ddots & \vdots \\ \varphi_1\left(\mathbf{r}_N; \eta_N\right) & \cdots & \varphi_N\left(\mathbf{r}_N; \eta_N\right) \end{vmatrix} \end{aligned} \tag{3}$$

where the φ_j are single-particle orbitals with compound (spatial and spin) index *i* and respective spatial and spin coordinates **r** and η. The φ_j are of course unique (otherwise Φ would vanish) and are taken to be orthonormal. In general, the solution of the time-independent Schrödinger equation for Hamiltonian (2) is a superposition of Slater determinants (3), and indeed, more than one basis state is required to describe many phenomena, excitons, for example. Intuition suggests, however, that the dominant single-particle properties of solids may be described by a single basis state (3). Obtaining the best possible single-Slater determinant solution involves minimizing $\langle \Phi | H | \Phi \rangle$ with respect to arbitrary variations of the φ_j and leads to the Hartree-Fock equations, as in atomic and molecular physics. In coordinate-space notation these are:

$$\begin{aligned} &\left[\frac{-\hbar^2}{2m}\nabla^2 + V\left(\mathbf{r}\right)\right]\varphi_i\left(\mathbf{r};\eta\right) + \left[\frac{e^2}{4\pi\varepsilon_0}\sum_{j=1}^{N}\sum_{\eta'}\int \frac{\left|\varphi_j\left(\mathbf{r}';\eta'\right)\right|^2}{\left|\mathbf{r}-\mathbf{r}'\right|} d^3r'\right]\varphi_i\left(\mathbf{r};\eta\right) \\ &-\frac{e^2}{4\pi\varepsilon_0}\sum_{j=1}^{N}\left[\sum_{\eta'}\int \frac{\varphi^*{}_j\left(\mathbf{r}';\eta'\right)\varphi_i\left(\mathbf{r}';\eta'\right)}{\left|\mathbf{r}-\mathbf{r}'\right|} d^3r'\right]\varphi_j\left(\mathbf{r};\eta\right) \\ &= E_i\varphi_i\left(\mathbf{r};\eta\right) \end{aligned} \tag{4}$$

where the $j = i$ term has been included in both summations since its appearance in the first is exactly canceled by its presence in the second.

Since the Hamiltonian (2) lacks any explicit spin dependence, the φ_j may be taken to be spin orbitals, products of purely spatial and spin functions: $\varphi_i(\mathbf{r};\eta) = \psi_1(\mathbf{r})\,\delta_{\eta,\Sigma(i)}$, where $\Sigma(i)$ denotes the spin state of the composite index *i*. Note that if φ_j and φ'_j differ only in spin state (e.g., one is spin up and the other is spin down), $\psi_j(\mathbf{r}) = \psi'_j(\mathbf{r})$. Also, it is easily seen that only parallel spins contribute to the second sum in (4), so that the Hartree-Fock equations for spin orbitals now read:

$$\left[\frac{-h^2}{2m}\nabla^2 + V(\mathbf{r})\right]\psi_i(\mathbf{r}) + \left[\frac{e^2}{4\pi\varepsilon_0}\sum_{j=1}^{N}\int\frac{\left|\psi_j(\mathbf{r}')\right|^2}{|\mathbf{r}-\mathbf{r}'|}d^3r'\right]\psi_i(\mathbf{r})$$

$$-\frac{e^2}{4\pi\varepsilon_0}\sum_{\substack{j=1,\\ i,j\|}}^{N}\left[\int\frac{\psi^*{}_j(\mathbf{r}')\psi_i(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d^3r'\right]\psi_j(\mathbf{r}) = E_i\psi_i(\mathbf{r}) \tag{5}$$

The first electron-electron interaction term in (5) is referred to as the direct (or Hartree) term and represents the (repulsive) Coulomb potential due to the charge of all the electrons in the system; it is identical for all orbitals. The second electron-electron term is called the exchange term and differs depending upon the orbital. It can lower the total energy of the system, unlike the direct term. Exchange interactions are responsible for magnetism.

The Lagrange parameters E_i appearing in equation (5) are not merely mathematical objects: they also have physical meaning, given by Koopman's Theorem. The key assumption of the theorem is that for a large number of electrons, *N*, removing one electron (e.g., that occupying the *k*-th orbital) will not significantly alter the remaining (*N*-1) orbitals. Note that, as physically reasonable and intuitively satisfying as this is, it remains an assumption, for as is clear from equation (5) the orbitals of the *N* and (*N*-1)-electron systems are in general different. If, as is usually the case, this assumption holds, it follows directly from equation (5) that the difference in the total energy expectation value between the *N*-electron Slate determinant $|\Phi\rangle$ and the (*N*-1)-electron Slater determinant from which the *k*-th orbital has been removed, $|\Phi_-\rangle$, is just E_k.

Further approximations are required to reduce the problem to that of *N* identical, non-interacting (quasi) electrons, for the *N* Hartree-Fock equations (5) are not identical due to the exchange term. Slater has suggested several approximations for dealing with this difficulty, including replacing the exchange term by a potential proportional to the cube root of the total electron density, motivated by the solution of the free-electron Hartree-Fock equations. Alternatively, he suggests replacing the exchange term by a weighted average over orbital probability density. Regardless of the particular approximation employed, the result is *N* identical single-electron problems

$$\frac{-\hbar^2}{2m}\nabla^2\psi(\mathbf{r})+V(\mathbf{r})\psi(\mathbf{r})=E\psi(\mathbf{r}) \tag{6}$$

where in (6) $V(\mathbf{r})$ includes the electron-ion, direct, and (approximate) exchange potentials. Note that in the many-electron problem which lead to equations (6), the Pauli exclusion principle is explicitly integrated deep in the structure of the solution, as expressed in the construction of the Slater determinant, for any such determinant having a non-unique orbital (i.e., $\varphi_j = \varphi_k, j \neq k$) vanishes. It remains (although less obviously) in the case of the N identical non-interacting single (quasi) electron problems, equations (6). Here, in the non-interacting electron problem the Hamiltonian is a sum of N single-body operators, and hence there exists a single Slater determinant which is its *exact* eigenstate.

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Bibliography

Ching, W. Y. and Chun C. Lin (1975). Orthogonalized linear combinations of atomic orbitals: Application to the calculation of energy bands of SiIII. *Physical Review B* **12**(12), 5536. [This paper discusses a more first-principles application of the tight-binding method.]

Cohen, Marvin L. and James R. Chelikowsky (1989). *Electronic Structure and Optical Properties of Semiconductors*, 2nd. ed. New York: Springer-Verlag. [This book discusses both the pseudopotential method and specific results for a number of technologically important semiconductors in detail.]

Harrison, Walter A. (1979). *Solid State Theory*, New York: Dover. [This is one of the classic beginning graduate-level solid state texts. Chapter II, secs. 1-5 in particular give good discussions of such topics as Koopmans' theorem, the properties of energy bands, and energy band calculations.]

Jones, William L. and Norman H. March (1973). *Theoretical Solid State Physics*, Vol. 1. New York: Dover. [This graduate-level solid state textbook is more mathematically detailed than most, with a high level treatment of symmetries of energy bands.]

Kittel, Charles (1996). *Introduction to Solid State Physics*, 7th. ed. New York: Dover. [This is a senior-undergraduate level text, more accessible than the others cited here.]

Kittel, Charles and Herbert Kroemer (1980). *Thermal Physics*, 2nd ed. New York: W. H. Freeman. [This junior/senior-undergraduate level text provides an excellent introduction to statistical mechanics.]

Madelung, Otfried (1978). *Introduction to Solid State Theory*, trans. B. C. Taylor. New York: Springer-Verlag. [This is another beginning graduate-level solid state text, providing detailed treatments of the Hartree-Fock approximation as applied to solids, energy band characteristics, and properties of energy bands.]

Slater, J. C. and G. F. Koster (1954). Simplified LCAO Method for the Periodic Potential Problem. *Physical Review* **94**(6), 1498. [This is the classic paper on the empirical tight-binding method. Although there have been many developments in the method since the work of Slater and Koster, all modern treatments are its direct descendants.]

Weissbluth, Mitchel (1978). *Atoms and Molecules*. New York: Academic. [This is an excellent beginning graduate-level text with a detailed treatment of atomic and molecular physics. Although it does not discuss solids, the physics and many of the methods are directly relevant to solids.]

Biographical Sketch

Timothy B. Boykin, is currently Associate Professor in the Department of Electrical and Computer Engineering of the University of Alabama in Huntsville (UAH), Huntsville, Alabama, USA. He received the B.S. in Electrical Engineering, *summa cum laude*, from Rice University (Houston, Texas, USA) in 1987 and the M.S. (1988) and Ph.D. (1992) in Electrical Engineering from Stanford University (Stanford, California USA) under the supervision of Prof. James S. Harris, Jr. Dr. Boykin came to UAH as an Assistant Professor in September, 1992, was promoted to Associate Professor in August, 1997, and advanced to tenure in August, 1998. He is a member of the American Physical Society, the Institute of Electrical and Electronics Engineers, Sigma Xi, and the honor societies Phi Beta Kappa, Tau Beta Pi, and Eta Kappa Nu. Most recently he received the 2001 UAH Foundation Award for Research and Creative Achievement in Applied Research/Technology. Dr. Boykin's research mainly concerns band structure effects in semiconductor nanostructures such as quantum wells and resonant-tunneling diodes (RTDs); he is author or co-author of over forty refereed journal articles. His work includes the first numerically-stable multi-band tight-binding current-voltage calculations for realistic RTD structures (i.e., with long space-charge regions); quantification of the incompleteness in and reproducibility limits of tight-binding models; boundary conditions for nanostructures with one-dimensional quantum confinement; electromagnetic coupling in empirical tight-binding models; and treatment of strained crystals in the tight-binding method.