

Local Density Formalism Approach to Cohesive Properties of Solids: Diamond, BN, and LiF

ALEX ZUNGER AND A. J. FREEMAN

*Department of Physics and Astronomy, and Materials Research Center,
Northwestern University, Evanston, Illinois 60201, U.S.A.*

Abstract

Predictions of the local density formalism approach to cohesive properties of covalently bonded solids (diamond and cubic BN) and prototype ionic system (LiF) are described using results of our recently developed fully self-consistent numerical basis set LCAO-DVM approach. Comparisons with restricted Hartree-Fock results and experiments for cohesive energies and equilibrium lattice constants are presented. Some of the principal bonding mechanisms in these crystals are discussed in terms of the contributions of local exchange and correlation to the binding and the charge redistribution relative to the noninteracting atoms.

1. Introduction

Despite the manifold successes of energy band theory in describing a wide spectrum of solid state properties, the *ab initio* determination of cohesive energies and equilibrium lattice constants remains as a relatively unexplored and underdeveloped field of study. Thus, there has developed considerable interest in the application of the local density formalism (LDF) [1, 2] for the study of the ground state electronic properties of molecules and solids. Investigations of the cohesive properties of small molecules [3-5], metals [6], and rare-gas solids [7] have elucidated the possibilities of obtaining a reasonably accurate description of binding energies and equilibrium geometries by incorporating exchange and correlation effects directly into a one-body potential. Similar studies on compounds, ionic insulators, and covalent semiconductors are beset with the difficulties of having to consider the full (nonmuffin-tin) crystal potential and to explicitly account for charge redistribution and hybridization processes by means of a fully self-consistent treatment. Such effects cannot be conveniently treated within the standard Augmented Plane-Wave (APW) or Kohn-Korringa-Rostoker (KKR) techniques previously used for such studies.

We have recently developed [8, 9] the fully self-consistent numerical basis set linear combination of atomic orbitals (LCAO) discrete variational method (DVM) for treating ground and excited state properties of solids in the LDF approximation. This scheme permits the treatment of general (i.e., analytic or numerical) basis functions and crystal potentials, and the determination of fully self-consistent solutions of the LDF one-particle equations without restricting the iterative path to a superposition of spherical charge densities [4] or to muffin-tin models [6, 7]. We have demonstrated a rapid convergence of the self-consistent (SC) cycle when the treatment of the full crystal charge density is suitably apportioned between real-space and Fourier-transformed recipro-

cal-space parts and have indicated the large degree of variational flexibility offered by a nonlinearly optimized (exact) numerical atomic-like basis set. We have shown that all multicenter interactions as well as the nonconstant parts of the crystal potential are efficiently treated by a three-dimensional Diophantine integration scheme [10].

This paper is concerned with the predictions of the LDF method for the cohesive energy and equilibrium lattice constants in covalently bonded solids (diamond and its heteropolar isoelectronic analogue, cubic boron nitride) and a prototype ionic solid (LiF). It represents part of a detailed study we are pursuing into the ground state properties of various solids, including the relative role of exchange and correlation [11, 12]. Comparisons are made with the results of restricted Hartree-Fock calculations and with experiment.

2. Methodology

Since a detailed description of the method has been given previously [8, 9], we outline here only those aspects pertinent to the present study. Our purpose is to solve the local-density one-particle eigenvalue equation for a periodic solid:

$$\left\{ -\frac{1}{2} \nabla^2 + V[\rho(\vec{r})] \right\} \psi_j(\vec{k}, \vec{r}) = \epsilon_j(\vec{k}) \psi_j(\vec{k}, \vec{r}) \quad (1)$$

for band index j and Brillouin zone (BZ) wave vector \vec{k} . Here $V[\rho(\vec{r})]$ is the crystal one-body potential given as a functional of the self-consistent crystal charge density $\rho(\vec{r})$ and includes an electron-nuclear and electron-electron Coulomb term $V_{\text{coul}}[\rho(\vec{r})]$ (which includes the electron self-interaction) and a local exchange [2] $V_x[\rho(\vec{r})]$ and correlation [13] term $V_{\text{corr}}[\rho(\vec{r})]$.

We first assume a population-dependent superposition model for $\rho(\vec{r})$ made up of the free-ion (or free-atom) densities $\rho_\alpha(\vec{r}, \{f_{n,l}^\alpha, Q^\alpha\})$. These are obtained from a self-consistent numerical solution of the LDF one-particle equation with the assumed ionic central field occupation numbers $\{f_{n,l}^\alpha\}$ and net charge Q^α and are lattice-summed to yield $\rho_{\text{sup}}(\vec{r}, \{f_{n,l}^\alpha, Q^\alpha\})$. This initial density is used to obtain an initial guess for the crystal potential $V_{\text{sup}}[\rho_{\text{sup}}(\vec{r})]$ in terms of $V_{\text{coul}}[\rho_{\text{sup}}(\vec{r})]$ and $V_x[\rho_{\text{sup}}(\vec{r})] + V_{\text{corr}}[\rho_{\text{sup}}(\vec{r})]$. The long-range part of the screened Coulomb potential is calculated by the Ewald technique [14]. The crystal wave functions $\psi_j(\vec{k}, \vec{r})$ are then expanded in an LCAO form in terms of the Bloch functions $\Phi_{\mu\alpha}(\vec{k}, \vec{r})$ defined by (the μ th orbital) basis functions $\chi_\mu^\alpha(\vec{r})$ on lattice site α . These basis functions are taken as exact numerical solutions of the single-site LDF one-particle equations for the assumed occupations and charges $\{f_{n,l}^\alpha, Q^\alpha\}$. For first-row atoms we use the $1s$, $2s$, $2p$, $3s$, and $3p$ orbitals for the band calculations, while for total energy calculations, we add $3d$ orbitals.

The matrix elements of $V_{\text{sup}}[\rho_{\text{sup}}(\vec{r})]$ in the Bloch basis $\Phi_{\mu\alpha}(\vec{k}, \vec{r})$ are evaluated by direct three-dimensional Diophantine numerical integration [10] without any shape approximation to the potential and include *all* the overlap and multicenter integrals between orbitals on lattice sites separated by less than 23 a.u. The secular equations are diagonalized for a set of six to ten special \vec{k} -points

in the irreducible BZ [15] and the linear LCAO expansion coefficients $C_{\mu\alpha j}(\vec{k})$ are used to construct the output crystal density $\rho_{\text{cry}}(\vec{r})$. Convergence tests for the radius of real-space lattice sums, the BZ sums, and the basis set expansion have assured an overall stability of the eigenvalues to within 0.05 eV over the entire band structure range studied.

We then start a two-stage iterative self-consistent (SC) procedure: in the first stage $\{f_{n,l}^{\alpha}, Q^{\alpha}\}$ are varied iteratively to minimize the difference $\Delta\rho(\vec{r}) = \rho_{\text{cry}}(\vec{r}) - \rho_{\text{sup}}(\vec{r}, \{f_{n,l}^{\alpha}, Q^{\alpha}\})$ in the least squares sense over the unit cell space where the basis set $\chi_{\mu}^{\alpha}(\vec{r})$ and the potential $V_{\text{sup}}[\rho_{\text{sup}}(\vec{r})]$ are optimized accordingly at each iteration (about 4–6 iterations are needed). After $\Delta\rho(\vec{r})$ has been minimized by selecting the optimum superposition model in terms of $\{f_{n,l}^{\alpha}, Q^{\alpha}\}$, we project in the second stage of self-consistency the residual $\Delta\rho(\vec{r})$ onto a set of symmetrized plane waves and solve the associate Poisson equation analytically in terms of the projected coefficients $\Delta\rho(\vec{K}_s)$ for a list of reciprocal lattice vectors \vec{K}_s . This reciprocal space expansion converges rapidly (7–17 stars of \vec{K}_s are needed) because the residual $\Delta\rho(\vec{r})$ is prepared to be spatially smooth. The correction to the Coulomb interelectronic potential $\Delta V(\vec{r})$ is then added to the $V_{\text{sup}}[\rho_{\text{sup}}(\vec{r})]$ obtained in the final iteration of stage 1 and this new Hamiltonian is diagonalized. The iterations in stage 2 are carried out so as to diminish the residual $\Delta\rho(\vec{K}_s)$ to a prescribed tolerance of $10^{-5}e$ (3–6 iterations are needed).

The calculation of the total crystal energy per unit cell is based on the LDF total energy expression and uses the final crystal density $\rho_{\text{cry}}(\vec{r})$. As described previously [8], the various terms appearing in this expression must be grouped so that the divergencies in the individual electron–electron and electron–nuclear energies per unit cell are canceled. We have also shown how the kinetic and Coulomb terms are combined in real space before their integration is attempted so as to affect a substantial numerical cancellation. Again three-dimensional Diophantine integrations are needed to obtain quantities such as $\int \rho_{\text{cry}}(\vec{r}) V[\rho(\vec{r})] d\vec{r}$ which converge more slowly than those necessary in the band structure study (although the convergence rate is better than in analogous molecular studies [5]). For example, in LiF a large number of Diophantine integration points (2000 per Li and 3000–4000 per F) together with an improved sampling point mapping scheme are needed in order to obtain an accuracy of 0.5–0.8 eV in the total energy. However, in diamond, we are able to obtain an accuracy of 0.2 eV by using some 10–30 Diophantine integration points inside the nuclear volume, about 300 integration points in the 1s orbital sphere, and 3500 points per atom in the rest of the unit cell volume. Since the BZ dispersion of the total orbital charge density $\rho(\vec{r}, \vec{k}) = \sum_j^{\text{occ}} n_j |\psi_j(\vec{k}, \vec{r})|^2$ is rather small [12], the use of only 10 \vec{k} -points in sampling $\rho(\vec{r}, \vec{k})$ introduces only small errors (0.2% in $\rho(\vec{r})$).

3. Results and Comparison with Experiment

Table I presents our LDF results for the binding energy (E_B) and equilibrium lattice constants (A_{eq}), and, for comparison, those values calculated by the restricted Hartree–Fock (HF) model [16–18] and the available experimental data

[19–23]. The values of the atomic total energies for C, B, and N are obtained from a spin-polarized local-spin density calculation [24] using the functional [3] that approaches the Singwi et al. [13] result in the nonspin-polarized limit. The corresponding values for the closed-shell Li^+ and F^- ions are obtained by a direct integration of the LDF total energy expression. The LDF model is seen to predict somewhat too low a binding energy (up to 7.5% for LiF) and too long a bond length (by 0.3–2%). The HF model, on the other hand, seems to yield too short a bond length. It is expected that those correlation corrections not present in both models (i.e., dispersion forces that are present even at the limit of nonoverlapping ions and arise from high-order perturbation terms involving excitations of virtual states) will act to further stabilize the crystal over the noninteracting atoms, and to yield, thereby, better agreement of the LDF results with experiment but too small A_{eq} for the HF predictions. Both the HF and the LDF results show the predicted trend of decreasing binding and increasing lattice constant with increasing ionicity in the system (Pauling's electronegativity differences between the atoms in the cells are 0.0, 1.0 and 3.0 for diamond, BN, and LiF, respectively). Our charge analyses of the ground state bands for these materials [12] predict about 35 and 100% charge transfer in BN and LiF, respectively.

Analysis of the binding in these systems [9, 11, 12] has revealed the following features:

(1) The correlation potential appearing in the LDF one-particle equations [13] has the effect of increasing the charge localization both in the core region and in the bond center region at the expense of deleting substantial charge from the back-bond region. This results in an increase of the binding energy by a few percent [9].

(2) In a self-consistent minimal basis set description of the covalent compounds, substantial density is shifted from the core region into the bond region (having a less attractive potential) to yield a reasonable description of the valence charge (as judged from the agreement with the low-angle x-ray scattering factor data [25]). However, only an extended basis set (including ion-pair functions)

TABLE I. Binding energies (E_B) and equilibrium lattice constant (a_{eq}) of diamond, boron nitride, and lithium fluoride calculated by the restricted Hartree-Fock (HF) and the present local density formalism (LDF) model. Zero point energy corrections to the observed binding energies were done by means of a Debye formula.

System	E_B (eV/pair)			a_{eq} (Å)		
	HF	LDF	Exp	HF	LDF	Exp
diamond	9.25 ⁽¹⁶⁾	15.6	15.24 ⁽¹⁹⁾	3.547 ⁽¹⁷⁾	3.581	3.567 ⁽²⁰⁾
BN	10.60 ⁽¹⁶⁾	12.8	≈13.0 ⁽²¹⁾	--	3.652	3.615 ⁽²²⁾
LiF	11.16 ⁽¹⁸⁾	9.8	10.6 ⁽²³⁾	3.972	4.093	4.018 ⁽²³⁾

is capable of producing a reasonable binding energy by restoring the density in the core region at the expense of the diffuse charge in the back-bond space.

(3) In the most ionic case studied (LiF), a large part of the binding ($\sim 80\%$) is contributed by the electrostatic Madellung field, so that, for the observed lattice constant, a reasonable binding energy is obtained even at the minimal basis set level. On the other hand, the calculated equilibrium lattice constant depends critically on the basis-set sensitive repulsive (short-range Coulomb) field, and only an extended set is capable of accurately reproducing this quantity.

(4) In contradiction with the conventional picture [26], we find, in the covalent systems, substantial penetration effects of the orbitals on a given site into the core region of neighboring sites. In the absence of such effects (e.g., by using artificially short-range basis orbitals) we find, together with the correct buildup of charge in the bond region, a dramatic lowering ($\sim 30\%$) in the binding energy. These penetration effects are induced largely by the basis orbitals that are unoccupied in the free atom ($3s, 3p$ for first-row atoms) and are slightly admixed into the ground state of the solid. Similarly, we find in LiF that the Li^+ virtual orbitals ($2s, 2p$) are responsible for a nonnegligible amount of charge in the interionic region ($0.15e/\text{\AA}^3$ at the bond center, compared with the observed [27] values of $0.15\text{--}0.19e/\text{\AA}^3$) while a simple description of the solid in terms of the closed-shell ion orbitals (Li^+ $1s$ and F^- $1s, 2s,$ and $2p$) would predict almost vanishing density in the bond center. The correct description of this charge buildup is found to be essential for an accurate estimate of the equilibrium lattice constant.

(5) For BN, we find that while the *static ionicity* Q (obtained here by a least-squares projection of the variational crystal density onto a set of ionic charge densities with fractional charges Q_B and Q_N) is rather low ($B^{+0.35}N^{-0.35}$), a rather different picture emerges from the study of the *dynamic ionicity* [28]. We have calculated the unit cell dipole moment $\bar{\mu}$ (by direct integration of $\bar{r}\cdot\rho(\bar{r})$) for a series of atomic positions related to each other by a symmetric displacement mode (i.e., the $\bar{q} = 0$ optical mode) and have then differentiated $\bar{\mu}$ to obtain the dynamic effective charge $e_T^* = 2.85e$ (compared with the value of $2.47e$ deduced from the infrared spectra [29]), which is substantially larger than the static value of $\sim 0.35e$. The ionicity of this system is hence substantially larger in the dynamic limit than can be inferred from simple consideration of the static ground state wave functions.

We close this discussion by commenting on the Gordon–Kim model [30] for binding in ionic solids as applied to the present study on LiF. The main assumptions of this model are: (i) E_B is assumed to be the sum of the point-ion electrostatic term and a pairwise additive ion–ion central potential $V_{ab}(\bar{r})$ summed over nearest-neighbors only. This neglects the predominantly repulsive three-center interaction terms present in our model. (ii) The electron–electron Coulomb part of $V_{ab}(\bar{r})$ is calculated from an overlapping superposition of free-ion HF charge densities (i.e., nonself-consistent model). This implies the neglect of the ion–ion orthogonality terms, the approximation that the individual ionic charges are not radially distorted in the interacting system, and that the

ground state HF orbitals are suitable as a basis for treating interactions in the LDF model. (iii) The kinetic energies of both the interacting system and the individual ions are calculated from a noninteracting homogeneous electron gas formalism (i.e., proportional to $\rho^{2/3}(\vec{r})$ with no gradient corrections). This omits the important (predominantly repulsive) contribution of the nonhomogeneous system and hence tends to overestimate E_B and to underestimate A_{eq} . (iv) The LDF is used to calculate the non-Coulombic part of $V_{ab}(\vec{r})$; long-range dispersion forces are neglected.

The approximations made in i and iii tend to omit repulsive interactions while approximation ii and the neglect of dispersion forces iv omit an essentially attractive interaction. The effect of approximation i can be roughly estimated using Kim's model for three-body forces [31] and next nearest-neighbor terms, while the effect of approximation ii can be estimated from studies on scaling the HF ionic wave functions [32]. These errors seem to be of roughly the same order (the omitted repulsive potential being slightly larger) and tend to cancel each other. The long-range dispersive interactions in LiF close to the equilibrium distance are rather small (~ 0.15 eV/pair [23]). Thus, the net effect of these approximations (i + ii + iii), seems to be the neglect of repulsive kinetic and potential terms which leads to overbinding. Gordon and Kim's [30] results for LiF (A_{eq} of 3.86 Å and E_B of 11.3 eV/pair) indeed confirm this conclusion. Further analysis of the model was carried out to understand the nature of the omitted repulsive terms. We have calculated the total energy of a LiF crystal using a nonself-consistent *superposition density* made up from free-ion local density orbitals. The potential energy terms PE (Coulomb exchange and correlation) were directly calculated from this density, while the kinetic energy term KE was calculated from the homogeneous gas equation ($KE \propto \rho^{2/3}(\vec{r})$). Approximation i is then practically eliminated. The result (at the observed lattice constant) showed that the kinetic contribution to E_B was 2.8 eV smaller (less positive) than the corresponding contribution calculated with the full Laplacian form, while the potential contribution was 0.8 eV larger (less negative) than that calculated from the (nonself-consistent) crystal wave functions. This leaves a net overbinding of 2 eV, in agreement with the arguments discussed above. Thus, the success of this model appears to stem, in part, from the partial balancing between the omitted repulsive kinetic terms iii and the attractive potential terms ii.

When approximation ii is removed (by using a self-consistently optimized charge density to compute KE and PE), we find a new type of cancellation: the kinetic energy contribution to E_B increases (mainly due to the contraction in the anion wave function) while the potential contribution decreases (i.e., PE becomes more negative, mainly due to shift of charge into the attractive core region) leaving a net overbinding of only 1.3 eV due to the omission of repulsive kinetic terms in iii. Finally, when approximation iii is also removed (i.e., in a fully self-consistent calculation using the Laplacian form for KE , of Table I) one obtains some *underbinding*, presumably due to the neglect of high-order correlation contributions iv. Thus, it seems that in order to obtain better agreement with experiment in a simple Gordon-Kim model, one should relax the underlying

approximations in a carefully *balanced* manner (e.g., replacement of the nearest-neighbor superposition density by a variationally calculated crystal density). However, it is stressed that, in such a model, even a variationally chosen density would still leave out some of the (gradient) kinetic contributions which can be incorporated fully only in a detailed calculation as that reported here.

Acknowledgment

Part of these computations were performed at the ASD Computer Center at Wright-Patterson Air Force Base, Dayton, Ohio. The authors are grateful to the staff for their cooperation. This research was supported by the National Science Foundation Grants Nos. DMR 76-81719 and 76-01057 and the Air Force Office of Scientific Research Grant No. 76-4928.

Dedication

This paper is dedicated to Professor P. O. Löwdin, a pioneer in the theory of cohesive properties of solids, on the occasion of his 60th birthday.

Bibliography

- [1] P. Hohenberg and W. Kohn, *Phys. Rev.* **136**, 864 (1964).
- [2] W. Kohn and L. J. Sham, *Phys. Rev.* **140**, 1133 (1965).
- [3] O. Gunnarsson, P. Johansson, S. Lundquist and B. I. Lundquist, *Int. J. Quant. Chem.* **S9**, 83 (1975).
- [4] H. Sambe and R. H. Felton, *J. Chem. Phys.* **62**, 1122 (1975).
- [5] E. J. Baerends and P. Ros, *Chem. Phys.* **2**, 52 (1973).
- [6] J. F. Janak, V. L. Moruzzi and A. R. Williams, *Phys. Rev. B* **12**, 1757 (1975).
- [7] J. R. Sabin, J. P. Worth and S. B. Trickey, *Phys. Rev. B* **11**, 3658 (1975).
- [8] A. Zunger and A. J. Freeman, *Int. J. Quant. Chem.* **S10**, 383 (1976).
- [9] A. Zunger and A. J. Freeman, *Phys. Rev. B* **15**, 4716 (1977).
- [10] C. B. Haselgrove, *Math. Compt.* **15**, 373 (1961); G. S. Painter, D. E. Ellis and A. R. Lubinsky, *Phys. Rev. B* **4**, 3610 (1971).
- [11] A. Zunger and A. J. Freeman, *Phys. Rev. B* **15**, 5049 (1977).
- [12] A. Zunger and A. J. Freeman, unpublished.
- [13] K. S. Singwi, A. Sjölander, P. M. Tosi and R. J. Land, *Phys. Rev. B* **1**, 1044 (1970).
- [14] P. P. Ewald, *Ann. Phys.* **64**, 753 (1971).
- [15] D. J. Chadi and M. L. Cohen, *Phys. Rev. B* **8**, 5747 (1973).
- [16] R. N. Euwema, G. T. Surratt, D. L. Wilhite and G. G. Wepfer, *Phil. Mag.* **29**, 1033 (1974).
- [17] G. T. Surratt, R. M. Euwema and D. L. Wilhite, *Phys. Rev. B* **8**, 4019 (1973).
- [18] R. N. Euwema, G. G. Wepfer, G. T. Surratt and D. L. Wilhite, *Phys. Rev. B* **9**, 5749 (1974).
- [19] H. D. Hagstrum, *Phys. Rev.* **72**, 947 (1947); *JANAF Tables of Thermochemical Data*, D. R. Stull, Ed. (Dow Chemical Co., Midland, Mich., 1965).
- [20] J. Thewlis and A. R. Davey, *Phil. Mag.* **1**, 409 (1968).
- [21] The cohesive energy of cubic BN can only be roughly estimated from the available experimental data. The heat of formation from gaseous N₂ and crystalline boron was determined [A. S. Dworkin, D. J. Sasmar and E. R. Van Artsdalen, *J. Chem. Phys.* **22**, 837 (1954); see also G. Berl and W. E. Wilson, *Nature* **191**, 380 (1961)] to be 60.7 ± 0.7 kcal/mol at 298°K. Correcting for the atomization energy of nitrogen and boron [L. Pauling, *The Nature of the*

Chemical Bond (Cornell Univ. Press, Ithaca, N.Y., 1960)] for cooling to 0°K [data from D. R. Stull, Ed., *JANAF Tables of Thermochemical Data* (Dow Chemical Co., Midland, Mich., 1965)] and finally for the zero point energy of the solid [using a Debye equation with $\theta_D = 1700^\circ\text{K}$ using data given by P. J. Gielisse, S. S. Mitra, J. N. Plendl, R. D. Griffis, L. C. Mansur, R. Marshall and E. A. Pascoe, *Phys. Rev.* **155**, 1039 (1967)] one obtains an estimate of 13 eV/pair for the static binding energy. The accuracy of this quantity is at present difficult to assess.

- [22] R. H. Wentrof, *J. Chem. Phys.* **26**, 916 (1957).
- [23] M. P. Tosi, *J. Phys. Chem. Solids* **24**, 965 (1963); F. G. Fumi and M. P. Tosi, *ibid.* **25**, 31, 45 (1964).
- [24] O. Gunnarsson, private communication (for which the authors are grateful).
- [25] G. Gottlicher and E. Wölfel, *Z. Electrochem.* **63**, 891 (1959); M. Renninger, *Acta Crystallogr.* **8**, 606 (1955).
- [26] C. Kittel, *Introduction to Solid State Physics*, 3rd ed. (John Wiley & Sons, New York, 1967).
- [27] J. Krug, H. Witte and E. Wölfel, *Z. Phys. Chem.* **4**, 36 (1955).
- [28] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford Univ. Press, Oxford, 1954), pp. 219 and 321.
- [29] G. Lucovsky, R. M. Martin and E. Burstein, *Phys. Rev. B* **4**, 1367 (1971).
- [30] R. G. Gordon and Y. S. Kim, *J. Chem. Phys.* **56**, 3122 (1972); Y. K. Sik and R. G. Gordon, *Phys. Rev. B* **9**, 3548 (1974).
- [31] Y. S. Kim, *Phys. Rev. A* **11**, 804 (1975).
- [32] J. Yamashita, *J. Phys. Soc. Jpn.* **7**, 784 (1957); K. Mansikka and F. Bystrand, *J. Phys. Chem. Solids* **27**, 1073 (1966).

Received February 22, 1977