PHYSICAL REVIEW B VOLUME 26, NUMBER 8 15 OCTOBER 1982

Total-energy all-electron density functional method for bulk solids and surfaces

M. Weinert, E. Wimmer,* and A. J. Freeman
Physics Department, Northwestern University, Evanston, Illinois 60201

(Received 1 June 1982)

A new formalism for determining highly accurate total energies of solids within density functional theory is presented in which all necessary terms are easily obtained from the energy-band calculation. A major feature of this all-electron approach is the explicit algebraic cancellation of the nuclear Coulomb singularities in the kinetic and potential energy terms which leads to good numerical stability. As an illustration, the method is implemented in the full-potential linearized augmented-plane-wave method for thin films and applied to monolayers of Cs and graphite. The structural information (lattice parameters, force constants, etc.) for graphite are found to be in very good agreement with experiment on bulk graphite and to be rather insensitive to the quality of the basis. The calculated cohesive energy (relative to a spin-polarized local-density atom), on the other hand, is quite sensitive to the quality of the basis; a limited basis yields results in fortuitous agreement with experiment. The converged result for the cohesive energy is found to be 17% too large compared to experiment, an error which appears to arise from the neglect of correlation with near-lying excited configurations in the local-density atom and not to errors in the condensed system.

I. INTRODUCTION

The intense experimental interest in surface problems such as chemisorption, surface reconstruction and relaxation, and dynamics has produced a wealth of data, much of it still not understood. Complicating the theoretical understanding is the fact that often the important structural parameters needed are not available experimentally. In order to circumvent this problem theoretically, one can use the general principle of minimization of the total energy to determine the stability of a system. Density functional theory[1,2] provides an elegant framework in which the total energy of solid-state systems can be obtained for any geometrical configuration of the nuclei. With the advent of accurate methods to solve the local-density[2] (LD) one-particle equations, there has been increasing interest[3-9] to use these methods to determine the total energy and related properties, such as equilibrium phases, lattice constants, and force constants of both bulk solids and surfaces.

The major problem in any straightforward application of the total-energy expressions involves numerical problems arising from the cancellation between the very large kinetic and potential-energy contributions.[3] The problem obviously becomes more severe for heavier atoms since the (chemically inactive) core electrons are responsible for the largest part of the total energy. To avoid this problem, one successful approach has been to remove the core electrons from the problem, as is done in the pseudopotential method[6]; within an all-electron approach, using the muffin-tin approximation,[4] Janak[3] has obtained an algebraic cancellation of part of the core contributions in the expressions for the total energy and pressure.

In this paper we go beyond these treatments and consider the total energy using an all-electron, general potential approach. In Sec. II we present a formalism that is easy to implement using quantities readily obtained from self-consistent band-structure calculations. A key feature of this new approach is the high accuracy that results from an explicit cancellation of the Coulomb singularities in the kinetic and potential-energy terms arising from the nuclear charge. As an example of the applicability of the method to solid-state systems, we have implemented it in our full-potential linearized augmented-plane-wave (FLAPW) method[10] for thin films. Results are presented for two different systems: a monolayer of a high-atomic-number metal, Cs, and a monolayer of covalently bonded graphite for which comparisons of the calculated equilibrium structural properties and cohesive energy can be made with experiment.

II. FORMALISM

A. General formulation

The total energy of a periodic solid (with frozen nuclear positions) within the density functional[1,2] framework is given by a sum of kinetic, potential, and exchange-correlation terms,[2]

$$E[\rho]=T_s[\rho]+U[\rho]+E_{\mathrm{xc}}[\rho]\ . \tag{1}$$

The kinetic energy is defined to be the kinetic energy of a noninteracting electron gas of the same density and is given by[3]

$$T_s[\rho]=\sum_i \int \psi_i^*(\vec{r})K_{\mathrm{op}}\psi_i(\vec{r})d\vec{r}\ . \tag{2}$$

The one-particle kinetic energy operator is given nonrelativistically (relativistically) in the standard way (with $\hbar=e=m=1$) by $-\frac{1}{2}\nabla^2(\vec{\alpha}\cdot\vec{p})$. The ψ_i's of Eq. (2) are solutions of the effective one-electron Schrödinger (or Dirac) equation[2]

$$[K_{\mathrm{op}}+V_{\mathrm{eff}}(\vec{r})]\psi_i(\vec{r})=\epsilon_i\psi_i(\vec{r}) \tag{3}$$

which defines the density in the standard way

$$\rho(r)=\sum_i \psi_i^*(r)\psi_i(r)\ ,$$

with the sums in the kinetic energy and the density taken over occupied states. The effective potential operator is the sum of the Coulomb potential $V_c(\vec{r})$ and the exchange correlation potential $\mu_{\mathrm{xc}}(\vec{r})$,

$$V_{\mathrm{eff}}(\vec{r})=V_c(r)+\mu_{\mathrm{xc}}(\vec{r})\ .$$

The potential energy $U[\rho]$ is the (classical) interaction energy between all charges in the system, electron-electron, electron-nuclear, and nulcear-nuclear interactions:

$$U[\rho]=\frac{1}{2}\left[\int \frac{\rho(\vec{r})\rho(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}d\vec{r}\,d\vec{r}\,' -2\sum_\alpha Z_\alpha \int \frac{\rho(\vec{r})d\vec{r}}{|\vec{r}-\vec{R}_\alpha|} +\sum_{\alpha,\beta}{}' \frac{Z_\alpha Z_\beta}{|\vec{R}_\alpha-\vec{R}_\beta|}\right], \tag{4}$$

where Z_α is the nuclear charge at $\vec{R}_\alpha$. Since the Coulomb potential at $\vec{r}$ is given by

$$V_c(\vec{r})=\int \frac{\rho(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}d\vec{r}\,'-\sum_\alpha \frac{Z_\alpha}{|\vec{r}-\vec{R}_\alpha|}\ , \tag{5}$$

we can write (assuming N unit cells of volume Ω in the crystal)

$$U=\frac{N}{2}\left[\int_\Omega \rho(\vec{r})V_c(\vec{r})d\vec{r}-\sum_\nu Z_\nu V_M(\vec{\gamma}_\nu)\right] \tag{6}$$

where the sum on ν runs over nuclei at $\vec{\gamma}_\nu$ in the unit cell. We have defined a generalized Madelung potential $V_M(\vec{\gamma}_\nu)$ as

$$V_M(\vec{\gamma}_\nu)=\int \frac{\rho(\vec{r})d\vec{r}}{|\vec{r}-\vec{\gamma}_\nu|}-\sum_\alpha{}' \frac{Z_\alpha}{|\vec{R}_\alpha-\vec{\gamma}_\nu|}\ , \tag{7}$$

i.e., the Coulomb potential at $\vec{\gamma}_\nu$ due to all charges in the crystal except for the nuclear charge at this site. In the solution of Poisson's equation, which we are using,[11] this is a simple term to obtain. The result is general and follows from the analysis of Ref. 11.

Assume that we have the Coulomb potential due to all charges in the crystal; then, in particular, we have the value on a sphere with radius R_ν centered at $\vec{\gamma}_\nu$. Let the spherical average of the potential be denoted $S_0(R_\nu)$. Then the (average) potential on this sphere due to all charges but this nucleus is given by

$$S(R_\nu)=S_0(R_\nu)+Z_\nu/R_\nu\ . \tag{8}$$

Now, to find the Coulomb potential at $\vec{\gamma}_\nu$, we solve the Dirichlet boundary-value problem for a sphere with the use of the electronic density inside the sphere and $S(R_\nu)$.[11] [Since we want the potential at the center of the sphere, only the $l=0$ term contributes. For this reason, we considered only the spherical average $S(R_\nu)$ above.] Then, if we expand the density in the sphere in a spherical harmonic representation

$$\rho(\vec{r}_\nu)=\sum_{lm}\rho_{lm}(r_\nu)Y_{lm}(\hat{r}_\nu)\ , \tag{9}$$

we have

$$\begin{aligned} V_M(\vec{\gamma}_\nu)&=\frac{1}{R_\nu}[R_\nu S_0(R_\nu)+Z_\nu-Q_\nu]+\sqrt{4\pi}\int_0^{R_\nu} dr\, r\rho_{00}(r_\nu) \\ &=\frac{1}{R_\nu}[R_\nu S_0(R_\nu)+Z_\nu-Q_\nu]+\left\langle \frac{1}{r}\rho(\vec{r})\right\rangle_\nu\ , \end{aligned} \tag{10}$$

where Q_ν is the total electronic charge in the sphere. This new form of the generalized Madelung potential has several nice features, one of which is that it is easily determined from quantities obtained from the band-structure calculation.

A simple expression for the kinetic energy per unit cell can be obtained by multiplying Eq. (3) by ψ_i^*, integrating and summing over all occupied states to yield[3]

$$T_s[\rho]=\sum_i \epsilon_i-\int_\Omega V_{\text{eff}}(\vec{r})\rho(\vec{r})d\vec{r}=\sum_i \epsilon_i-\int_\Omega V_c(\vec{r})\rho(\vec{r})d\vec{r}-\int_\Omega \mu_{\text{xc}}(\vec{r})\rho(\vec{r})d\vec{r}\ . \tag{11}$$

Then the total energy per unit cell is

$$E=\sum_i \epsilon_i-\tfrac{1}{2}\int_\Omega \rho(\vec{r})[V_c(\vec{r})+2\mu_{\text{xc}}(\vec{r})]d\vec{r}-\tfrac{1}{2}\sum_\nu Z_\nu V_M(\vec{\gamma}_\nu)+E_{\text{xc}}[\rho]\ ,$$

which, using Eq. (10), simplifies to

$$E=\sum_i \epsilon_i-\frac{1}{2}\left[\int_\Omega \rho(\vec{r})V_c(\vec{r})d\vec{r}+\sum_\nu Z_\nu\left\langle \frac{1}{r}\rho(\vec{r})\right\rangle_\nu\right]-\int_\Omega \rho(\vec{r})\mu_{\text{xc}}(\vec{r})d\vec{r}$$
$$-\frac{1}{2}\sum_\nu \frac{Z_\nu}{R_\nu}[R_\nu S_0(R_\nu)+Z_\nu-Q_\nu]+E_{\text{xc}}\ . \tag{12}$$

In this form of the total energy, the Coulomb singularities of the nuclei in the potential are canceled explicitly when the terms in the large parentheses are combined. To see this, consider the spherical harmonic representation of the potential and density about each nucleus in the unit cell, as in (9). Then consider the term in the large parentheses centered about $\vec{\gamma}_\nu$,

$$\int \rho(\vec{r})V_c(\vec{r})d\vec{r}+Z_\nu\sqrt{4\pi}\int_0^R dr\, r^2\frac{\rho_{00}(r)}{r}=\sqrt{4\pi}\int dr\, r^2\rho_{00}(\vec{r})\left[V_{00}(r)Y_{00}(\hat{r})+\frac{Z_\nu}{r}\right]$$
$$+\sum_{lm>0}\int dr\, r^2\rho_{lm}(r)V_{lm}(r)\ .$$

The Coulomb singularity comes in only through $V_{00}(r)$, which can be written as the sum of the nuclear part, and a smooth, nonsingular part $\hat{V}_{00}(r)$ arising from the electrons

$$V_{00}(r)=-\sqrt{4\pi}\frac{Z_\nu}{r}+\hat{V}_{00}(r)\ .$$

From this form, it is obvious that we have canceled the Coulomb singularity. Note that this cancellation occurs only by combining the kinetic and potential-energy terms; each term taken separately has the singularity.

With the use of the standard local-density approximation, the exchange-correlation energy functional in Eq. (12) is expressed as

$$E_{\text{xc}}[\rho]\approx\int_\Omega \rho(\vec{r})\epsilon_{\text{xc}}(\vec{r})d\vec{r}\ . \tag{13}$$

B. Implementation via the FLAPW thin-film method

As our illustration of this new approach, we discuss its implementation via the FLAPW method for thin films.[10] This method has demonstrated its accuracy in a number of problems with reduced translational symmetry.[10,12] In the FLAPW method there are no shape approximations to the density or to the potential,[11] and all electrons are included; the core is treated fully relativistically, while the valence electrons are treated semirelativistically (neglecting spin-orbit interactions).

The FLAPW is a plane-wave-based method whose basis functions consist of radial functions and their energy derivatives inside the spheres, which are matched onto plane waves in the interstitial with continuous value and first derivative. This form of the basis functions results in high variational freedom and gives a systematic prescription for improving the basis.

Likewise, in the representation of the density and potential, we make use of the "natural" representations, which correspond to a Fourier expansion in the interstitial and a spherical harmonic representation in the sphere. Note that this division is purely for mathematical convenience. By extending the Fourier expansion

$$\rho(\vec{r})=\sum_{\vec{G}}\rho(\vec{G})e^{i\vec{G}\cdot\vec{r}},\quad \vec{r}\in \text{interstitial}$$

into the spheres and writing the plane-wave continuation in each sphere in an (l,m) representation

$$\bar{\rho}_{lm}(r_\nu)=4\pi i^l\sum_{\vec{G}}\rho(\vec{G})e^{i\vec{G}\cdot\vec{\gamma}_\nu}j_l(Gr_\nu)Y^*_{lm}(\vec{G})\ ,$$

we see that the total energy per unit cell of volume Ω is

$$E=\sum_i\epsilon_i-\sum_{\vec{G}}\Omega\rho(\vec{G})\tilde{V}^*(\vec{G})-\tfrac{1}{2}\sum_\nu\frac{Z_\nu}{R_\nu}[Z_\nu-Q_\nu+R_\nu S_0(R_\nu)]$$
$$-\sum_\nu\sum_{lm}\int_0^{R_\nu}dr\,r^2\left[\rho_{lm}(r_\nu)\left[\tilde{V}^*_{lm}(r_\nu)+\frac{\sqrt{4\pi}}{2r_\nu}Z_\nu\delta_{l0}\right]-\bar{\rho}_{lm}(\bar{r}_\nu)\bar{V}^*_{lm}(r_\nu)\right]\ , \tag{14}$$

where $\tilde{V}(\vec{r})$ and $\bar{V}_{lm}(\vec{r})$ are obtained from

$$\tilde{V}(\vec{r})=\tfrac{1}{2}V_c(\vec{r})-\epsilon_{\mathrm{xc}}(\vec{r})+\mu_{\mathrm{xc}}(\vec{r})\ . \tag{15}$$

Since these formulas are straightforward to modify for the surface or thin-film geometries, we do not give the explicit formulas but refer the reader to Refs. 10 and 13. Since we have analytically canceled the large contributions of the kinetic and potential-energy terms, we now expect good numerical stability, even when the core states are included. As we shall see, this expectation is borne out in practice even for systems with high atomic numbers.

III. APPLICATION TO METAL FILMS: Cs MONOLAYER

As a first test case we have determined the total energy as a function of lattice parameter for a high-Z metallic system, Cs. Since no comparison with experiment can be made in this case, we chose an unsupported square monolayer film as the simplest case with which to illustrate the implementation of the method to metallically bonded systems.

The charge density for each lattice parameter was obtained self-consistently on the same 10 k-point set in the irreducible wedge of the two-dimensional Brillouin zone. States were occupied according to a Fermi function corresponding to a temperature broadening of 0.005 mRy. (Since in this calculation we are interested in assessing our numerical stability for heavy metallically bonded systems, we have used a rather small k-point sampling and large temperature broadening.) The basis set included ~170 functions per k point. The potential and density were expanded inside the spheres in lattice harmonics with $l\leq 8$ and in the interstitial in 129 symmetrized plane waves.

The results are given in Fig. 1. Note that the scale of the figure is 1 mRy while the value is $\sim -155\,63$ Ry. A least-squares fit of our calculated values to a parabola gives a maximum deviation of 0.03 mRy, i.e., an internal numerical stability of one part in 10^9,[14] which makes calculations of surface systems composed of high-Z atoms feasible.

IV. APPLICATION TO GRAPHITE MONOLAYER

As stated, our motivation for determining the total energy is as a tool to treat problems primarily in surface physics. Because of the complexity of the problem it is important to demonstrate the accuracy of the method for systems that have experimentally known parameters. For this reason, we have chosen as an illustrative application, a graphite monolayer with which to test the applicability of our method for determining the ground-state properties of surfaces and thin films. Graphite is a layer compound that has very strong interactions in the plane, but only very weak interplane interactions, i.e., the structural parameters in the plane are nearly independent of crystal thickness.[15] In this way we

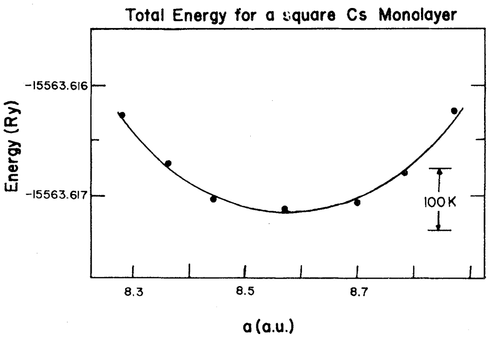

FIG. 1. Total energy vs lattice parameter for a square Cs monolayer.

will be able to compare our theoretical results for a monolayer of graphite with experiment on bulk graphite in order to assess our ability to treat interesting surface problems. Furthermore, since in the FLAPW method we have eliminated the standard approximations not inherent in LD theory, our results are also a test of the local-density approximation for exchange and correlation.

As in the case of the Cs monolayer, we consider an unsupported monolayer of carbon atoms, but now in both square and hexagonal lattices. Since we are interested in comparing two quite different geometries, it is important that the results are highly converged with respect to calculational parameters. We have used quite large basis sets ($\sim 150-200$ basis functions per atom) and have varied the k-point sampling set to check our convergence. We estimate that the absolute position of the curves in energy are converged to within 5 mRy, i.e., errors smaller than would arise by using a different exchange-correlation potential than the Hedin-Lundqvist parametrization[16] used here.

A. Structural information

A central question in the theory of cohesion is the relative stability of different crystal structures. For this reason we have determined the total energy per atom versus nearest-neighbor distance for both the square and hexagonal lattices. The results are presented in Fig. 2. As expected, the hexagonal lattice is energetically favored (by ~ 3.3 eV/atom) compared to the square lattice. The calculated equilibrium nearest-neighbor distances for the two lattice types are substantially different. However, the density of atoms is nearly the same: (the equilibrium planar) area per atom is 2.60 and 2.65 Å^2 for the hexagonal and square lattices, respectively. The calculated bond length for the hexagonal graphite monolayer of 2.450 Å is contracted by $\sim 0.4\%$ compared to the experimental value of 2.461 Å for bulk graphite.[15,17] That the monolayer is contracted with respect to the bulk is consistent with the experimental observation that the in-plane thermal expansion coefficient is negative below about 400 °C.[18,19] The explanation[18] that this effect is due to a lateral (Poisson) contraction caused by thermally stretching the crystal along the c axis, suggests that for the monolayer (with the interlayer spacing effectively infinite) there should also be a contraction. The amount of contraction for a monolayer cannot be estimated easily, but should be on the order of a few tenths of a percent (or ~ 0.006 Å, in this case). These arguments suggest that our agreement with experiment for the lattice constant is better than the 0.4% disagreement compared to bulk. Perhaps, more importantly, the results show that we are able to correctly predict the small contraction of the in-plane lattice parameter.

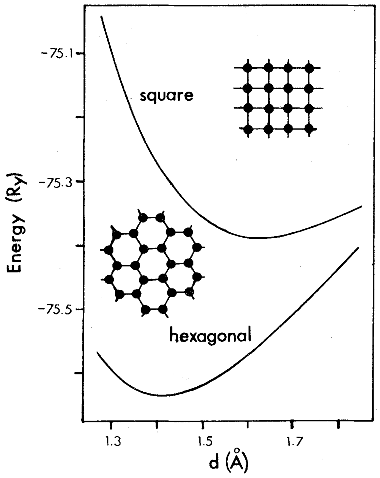

FIG. 2. Total energy per atom vs nearest-neighbor distance for square and hexagonal monolayers of carbon atoms.

We now turn our attention to the sensitivity of the structural information to the basis convergence. This investigation is important since calculations with a limited basis have been (and undoubtedly will be) reported. In Fig. 3 we show the total energy of the hexagonal monolayer using a limited basis (curve a) and a well-converged basis (curve b). The first point to notice is that both the shape and position of the minimum in each curve agree very well but are shifted in energy. For both cases the values of the calculated equilibrium lattice parameters and force constants[20–22] are compared with experiment in Table I. The calculated equilibrium lattice constants agree to within 1% of each other; however, the limited-basis value is expanded compared to both the converged-basis and experimental values. The calculated curvatures are in reasonable agreement with the experimental values, which are themselves model dependent.

The large degree of insensitivity of the structural information to basis convergence is of importance and somewhat surprising. The significance of this finding is that it shows that limited-basis results can give reasonable structural information, and hence if one is looking for the minimum in the total

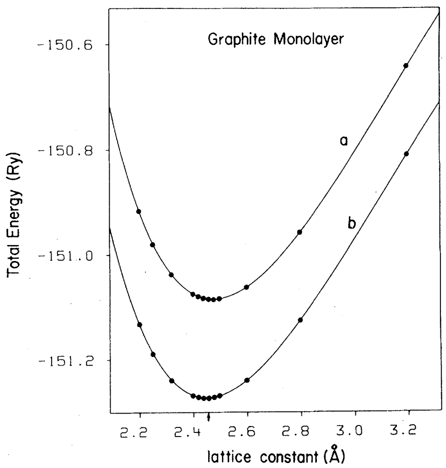

FIG. 3. Total energy per unit cell vs lattice constant for a hexagonal monolayer using *a* a limited basis and *b* a converged basis.

energy versus a single parameter, e.g., surface reconstruction or the absorbate equilibrium position, one does not need complete convergence of the basis, but only a reasonable basis. This result makes it possible to treat systems for which one must use a somewhat limited basis for practical reasons.

Related to this question of limited variational freedom is the frozen-core approximation: In this approximation the variational space for each core state is restricted to a single function obtained from another calculation. Use of the density and kinetic energy of the *C* atomic core has little effect on the total energy of the hexagonal graphite lattice: the differences in total energy are 0.016, 0.004, and 0.0008 eV for lattice parameters of 2.20, 2.46, and 3.20 Å, respectively. As expected from a variational argument,[23] the frozen-core results lie above the all-electron results with the differences decreasing with increasing internuclear separation.

TABLE I. Comparison of calculated structural information for different basis sets and experiment for graphite.

	Lattice constant (Å)	Curvature (eV/Å^2)
Limited basis	2.475	22.8
Converged basis	2.450	23.4
Experiment	2.461[a]	22.6[b]
		22.1[c]
		20.2[d]

[a] Reference 15.
[b] Reference 20.
[c] Reference 21.
[d] Reference 22.

B. Cohesive energy

Although the structural parameters are rather insensitive to basis convergence, the absolute position of the total-energy curve, and hence the cohesive energy, depends on the quality of the basis. The absolute values of the experimental and calculated LD total energies differ by ~10 eV/atom, which by comparing ionization potentials are seen to arise mainly from the self-energy of the 1*s* electrons. This problem of local density does not affect cohesive energies as can be seen from the frozen-core results where errors in the core are canceled explicitly. In Table II we compare the calculated cohesive energies (defined as the difference between the total energy per atom, corrected for the zero-point energy of the monolayer, and the spin-polarized free atom) with the experimental value. Since we are neglecting the interlayer binding, we would expect to obtain a slightly smaller cohesive energy (on the order of a few tenths of an eV) than is found for bulk graphite. What we find, however, is that the limited-basis result is in fortuitously excellent agreement with experiment, while the converged LD result is overbound by 1.3 eV/atom (an error of ~0.1% of the total energy per atom). The tendency for LD to overestimate the cohesive energy is in agreement with the results of Moruzzi, Janak, and Williams[4] on a large number of bulk metals. These authors suggest that the problem lies in the atomic calculations, a suggestion that we consider in detail for the carbon atom.

The ground state of the C atom is a ^3P state. (The multiplet structure for the $1s^2 2s^2 2p^2$ ground-state configuration consists of ^3P, ^1D, and ^1S terms.) While in a standard LD treatment one does not obtain the multiplet splitting, von Barth[24] has obtained for the C atom a lowering in energy of 1.20

TABLE II. Cohesive energy for graphite monolayer.

	E_B (eV/atom)	$E_{\text{theor}} - E_{\text{expt}}$ (eV/atom)
Limited basis	7.41	0.02
Converged basis	8.69	1.30
Experiment	7.39[a]	

[a] *Selected Values of Chemical Thermodynamic Properties,* Natl. Bur. Stand (U.S.) Circular 500 (U.S. GPO, Washington, D.C., 1952).

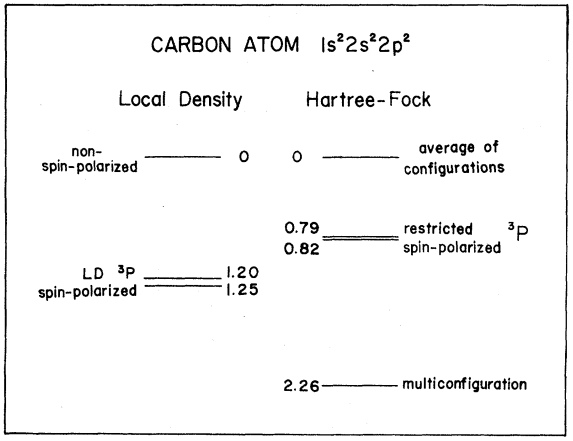

FIG. 4. Energy splittings of the carbon atom in local density and Hartree-Fock. The LD multiplet value is from Ref. 24, while all HF results are from Ref. 25. All energies are in eV and are relative to the non-spin-polarized (average-of-configurations) calculations for the LD (HF) results.

eV for the ^3P state compared to a non-spin-polarized LD calculation; this result should be compared to that of a spin-polarized LD calculation, which gives a lowering of 1.25 eV (cf. Fig. 4). [Spin-polarization projects out mainly the ^3P state while at the same time allowing (in this case small) extra variational freedom in the wave function.] Since it is difficult to determine where the remaining errors arise, we consider the corresponding Hartree-Fock case.

In Hartree-Fock (HF) it is easier to calculate and separate the effects of correlation. The HF results of Mallow[25] give lowerings of 0.79 and 0.82 eV for the ^3P state using restricted HF and spin-polarized HF, respectively, compared to the average-of-configurations result (essentially corresponding to the non-spin-polarized LD result). Now in many atomic systems, of which C is a notable example, accurate total energies result only when the interaction with near-lying excited-state configurations (configuration interaction) is included. For systems in which only a few such configurations play a dominant role, this type of correlation may be included by means of a multiconfiguration HF (MCHF) treatment. For C the important ^3P configurations are[25] $1s^2 2s^2 2p^2$, $1s^2 2p^4$, $1s^2(2s3d;{}^3D)(2p^2;{}^3P)$, and $1s^2(2s3d;{}^3D)(2p^2;{}^1D)$; the latter two configurations are important in that they provide so-called d-type radial correlation. As shown in Fig. 4 the MCHF results[25] are 2.26 eV lower than the average of configurations, i.e., ~1.4 eV lower than the spin-polarized results. From these results it is obvious that configuration-interaction-type correlation is important and that in LD we are making an error in the correlation energy of ~1 eV in the carbon atom compared to the extended system, graphite. If we use the results of the atom calculations as a rough guide, we would estimate a cohesive energy of ~7.6 eV, a value now in reasonable agreement with experiment.

V. CONCLUSIONS

We have presented a new formalism for total-energy calculations within the (local) density functional framework. The main features are that all necessary quantities are easily obtained from band-structure calculations and, more importantly, there is an explicit algebraic cancellation of the nuclear Coulomb singularities between the kinetic and potential-energy terms. This cancellation leads to good numerical stability, allowing one to treat the total energy of an all-electron system to high accuracy without resorting to frozen-core, pseudopotential, or other approximations.

In our application to the graphite monolayer, we find that structural information (lattice parameters, force constants, etc.) is obtained accurately and is found to be rather insensitive to the quality of the basis, while the cohesive energy, on the other hand, is quite sensitive to the basis convergence. The converged-basis results overbind the monolayer by ~1.3 eV/atom, whereas the limited-basis results give fortuitously excellent agreement with experiment; hence agreement in the cohesive energy should not be taken as a measure of the quality of a calculation. The error in the cohesive energy can be atrributed to errors in the local-density treatment of the atom, in particular, to the neglect of correlation with low-lying excited atomic states, which are not included in the treatment of the ground-state configuration.[26] Including a crude estimate of this term yields a cohesive energy in reasonable agreement with experiment. The results for the graphite monolayer show that the use of our total-energy formalism in conjuction with an accurate all-electron method such as the FLAPW leads to the accurate determination of structural parameters. The high degree of internal numerical stability allows one to treat even quite large systems composed of transition metals, thereby opening the possibility of accurately describing the energetics and dynamics of surface processes.

ACKNOWLEDGMENTS

We would like to thank S. Ohnishi, B. Delley, and H. Jansen for helpful discussions and J. V. Mallow for performing the Hartree-Fock calculations. The work of S. Ohnishi in sorting out the experimental force constants for graphite is gratefully acknowledged. This work was supported by the National Science Foundation (Grant No. DMR77-23776).

---

[*] Permanent address: Institut für Physikalische Chemie, University of Vienna, Währingerstr. 42, A-1090 Vienna, Austria.

[1] P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964).

[2] W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965).

[3] J. F. Janak, Phys. Rev. B 9, 3985 (1974).

[4] V. L. Moruzzi, J. F. Janak, and A. R. Williams, *Calculated Electronic Properties of Metals* (Pergamon, New York, 1978).

[5] A. Zunger and A. J. Freeman, Phys. Rev. B 15, 4716 (1977).

[6] J. Ihm, A. Zunger, and M. L. Cohen, J. Phys. C 12, 4409 (1979).

[7] J. Ferrante and J. R. Smith, Phys. Rev. B 19, 3911 (1978).

[8] H. Wendel and R. M. Martin, Phys. Rev. B 19, 5251 (1979).

[9] J. Callaway, X. Zou, and D. Bagayoko (unpublished).

[10] E. Wimmer, H. Krakauer, M. Weinert, and A. J. Freeman, Phys. Rev. B 24, 864 (1981).

[11] M. Weinert, J. Math. Phys. 22, 2433 (1981).

[12] M. Weinert, E. Wimmer, A. J. Freeman, and H. Krakauer, Phys. Rev. Lett. 47, 705 (1981); E. Wimmer, M. Weinert, A. J. Freeman, and H. Krakauer, Phys. Rev. B 24, 2292 (1981); E. Wimmer, A. J. Freeman, M. Weinert, H. Krakauer, J. R. Hiskes, and A. M. Karo, Phys. Rev. Lett. 48, 1128 (1982).

[13] H. Krakauer, M. Posternak, and A. J. Freeman, Phys. Rev. B 19, 1706 (1979).

[14] It should be pointed out that since the minimum is so flat that changing the number of k points or the temperature broadening results in shifts of the curve, but does not change our conclusion concerning the internal numerical stability.

[15] J. D. Donohue, *The Structure of the Elements* (Wiley, New York, 1974).

[16] L. Hedin and B. I. Lundqvist, J. Phys. C 4, 2064 (1971).

[17] The smaller value of $a = 2.456$ Å given in R. W. G. Wyckoff, *Crystal Structures* (Wiley, New York, 1963), Vol. 1, appears to be in error because of a change of units ($2.456 kx \approx 2.461$ Å).

[18] J. B. Nelson and D. P. Riley, Proc. Phys. Soc. London 57, 477 (1945).

[19] A. Ludsteck, Acta Crystallogr. Sect. A 28, 59 (1972).

[20] A. P. P. Nicholson and D. J. Bacon, J. Phys. C 10, 2295 (1977).

[21] J. A. Young and J. V. Koppel, J. Chem. Phys. 42, 357 (1965).

[22] O. L. Balkslee, D. G. Proctor, E. J. Seldin, G. B. Spence, and T. Weng, J. Appl. Phys. 41, 3373 (1970); E. J. Seldin and C. W. Nezbeda, *ibid.* 41, 3389 (1970).

[23] U. von Barth and C. D. Gelatt, Phys. Rev. B 21, 2222 (1980).

[24] U. von Barth, Phys. Rev. A 20, 1693 (1979).

[25] J. V. Mallow (private communication); J. V. Mallow and P. S. Bagus, J. Quan. Spectrosc. Radiat. Transfer 16, 409 (1976); P. S. Bagus and C. M. Mosser, J. Phys. B 2, 1214 (1969).

[26] In general, the neglect of this type of correlation should also similarly affect calculated (local-density) chemisorption energies of atoms and molecules. With the use of reference systems with correlations as similar as possible to the final adsorbed system, these discrepencies will be minimized; for example, to treat molecular adsorption, the reference systems should be the surface and the free molecule, not the constituent atoms. Likewise, because of better cancellation of correlation effects, we expect that dilute coverages and/or adsorption of larger molecules (which will be more overbound relative to the atom than similar smaller molecules) will yield local-density chemisorption energies in better agreement with experiment than will, for example, a dense atomic overlayer.