

Comparison of the Harris and the Hohenberg-Kohn-Sham functionals for calculation of structural and vibrational properties of solids

H. M. Polatoglou* and M. Methfessel†

*Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, Postfach 80 06 65,
D-7000 Stuttgart 80, Federal Republic of Germany*
and Fritz-Haber-Institut, Faradayweg 4-6, D-1000 Berlin 33, Federal Republic of Germany

(Received 16 October 1989)

The Harris energy functional and overlapped free-atom charge densities are used to perform total-energy calculations for Si and C. Accurate results are obtained for elastic constants and phonon frequencies. The energy-volume curves for different phases of Si are reproduced well if a slightly contracted free-atom charge density is used.

I. INTRODUCTION

Self-consistent total-energy calculations based on the Hohenberg-Kohn-Sham local-density approximation¹ have become an extremely useful tool, making possible parameter-free predictions for phonon frequencies, phase stabilities, equilibrium geometries, and many other quantities of interest. A key factor hereby is that the local-density model for the electron-electron interaction leads to total energies which are, in most cases, surprisingly accurate. In principle, it is thus possible to calculate the total energy for any given arrangement of atoms, to a good degree of precision, given only the atomic numbers and positions. However, in practice the technical difficulties are considerable so that systems containing more than about 50 atoms cannot normally be treated with state-of-the-art accuracy. In the local-density approach, it is necessary to solve coupled equations involving single-particle wave functions and an effective, density-dependent potential. These equations must be iterated to self-consistency by repeatedly solving the Schrödinger and Poisson equations. This procedure converges well for systems of only a few atoms, but unfortunately becomes increasingly unstable for complex systems. Consequently it is of interest to devise alternative schemes, based on the local-density approximation and of similar accuracy, which eliminate the time-consuming self-consistency cycle. These techniques would make possible efficient total-energy calculations for systems of considerably increased size and complexity. One such approach, using the Harris functional for the total energy,² has been tested previously for dimers^{2,3} and for cohesive properties of solids.⁴ In this paper, we demonstrate that very accurate results can also be obtained for phonons and elastic constants of diamond-structure Si and C. In addition, we discuss the phase stabilities and energy-volume curves obtained using the functional. A comparison is made to a similar approach used previously,⁵ which evaluates the local-density energy functional for the output density after the first iteration. A summary of parts of this work was presented in Ref. 6. Recently, a comparison of non-

self-consistent schemes was also presented in Ref. 7.

The starting point for simplified total-energy schemes is the variational principle of density-functional theory. The central quantity is the ground-state density $n(\mathbf{r})$ for the full many-particle wave function. It has been shown that (for a given external potential V_{ext} , and without spin polarization) there exists a functional of n which has the form

$$E[n] = \int d\mathbf{r} V_{\text{ext}}(\mathbf{r})n(\mathbf{r}) + F[n], \quad (1)$$

where $F[n]$ is universal, i.e., does not depend on V_{ext} . The energy functional is minimal at the true ground-state density; its value there is the ground-state total energy including electron exchange and correlation. Since the functional $F[n]$ is not known explicitly, it is usually approximated using the "local-density" form for the exchange-correlation part:

$$F[n] = T[n] + \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \int d\mathbf{r} n(\mathbf{r})\epsilon_{\text{xc}}(n). \quad (2)$$

Here, $T[n]$ is the kinetic energy for a system of noninteracting electrons with the same density and $\epsilon_{\text{xc}}(n)$ is chosen so that the correct many-body result is obtained for the interacting-free-electron gas. The standard self-consistent procedure is equivalent to a direct minimization of a functional $E[n]$ under the constraint of the electron number. Alternatively, due to the variational principle, a good estimate of the ground-state energy could be obtained if the functional were to be evaluated at a suitable trial density, which could be constructed by some simple prescription. The difficulty with this approach is that $T[n]$ cannot be evaluated unless n is assembled from wave functions which are solutions of the single-particle Schrödinger equation for some potential. While it is of importance for density-functional theory that such a potential must exist for reasonable choices of n , no prescription is known for finding it efficiently in practice. The problem can be avoided by instead using as the energy es-

timate $E[n_{\text{out}}]$, where n_{out} is the output density, obtained by solving the Schrödinger equation for the effective potential made from n . In fact, this is nothing more than the total energy after the first self-consistency iteration and this “one-shot” procedure for total energies has already been considered, e.g., in Ref. 5. We shall denote this energy by E_{KSI} . In this paper, we concentrate on an alternative energy functional suggested by Harris² and discussed by Foulkes.³ Harris introduced the following functional of the trial density:

$$E_H[n] = \sum_i a_i \bar{\epsilon}_i - \int d\mathbf{r} n(\mathbf{r}) \left[\frac{1}{2} \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \mu_{\text{xc}}(n) \right] + E_{\text{xc}}[n], \quad (3)$$

where n is the trial density, the $\bar{\epsilon}_i$ are the eigenvalues in the effective potential V_{eff} made using the trial density, the a_i are occupation numbers, $E_{\text{xc}}[n] = \int d\mathbf{r} n(\mathbf{r}) \epsilon_{\text{xc}}(n)$, and $\mu_{\text{xc}}(n)$ is the exchange-correlation potential. This functional can be shown to be stationary at the self-consistent density and to take the same energy value there. Therefore, it also has the property that an accurate estimate of the ground-state energy results for a trial density which is reasonably close to the self-consistent one. However, it has the advantage that the functional can be evaluated directly for any given trial density n without a search for the effective potential which yields n . The necessary steps are the following: an effective potential is constructed from the density, as is done in each iteration of the self-consistent procedure

$$V_{\text{eff}}(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \mu_{\text{xc}}(n) \quad (4)$$

and the sum of the occupied eigenvalues in this potential is calculated; then the electrostatic and exchange-correlation energies and $\int d\mathbf{r} n \mu_{\text{xc}}(n)$ for the input density are evaluated and added with the proper signs. The output density is not required. (Note that the internuclear repulsion energy must be added to both functionals.) As was suggested by Harris, it is natural to construct the trial density by overlapping spherical free-atom densities. In that case, the double-counting terms can be expressed to a good approximation as a sum of pairwise contributions.³ Thus, in addition to the self-consistency problem, the Harris functional avoids a number of steps which are time consuming in some methods; for example, the calculation of the eigenvectors and the task of expressing the output density in a form which permits the solution of the Poisson equation and evaluation of the exchange-correlation energy. Also, it seems to be a very good starting point for understanding empirical models. The relevant question for the utility of the Harris functional is whether the output energies are accurate enough. The first tests were done by Harris for a number of homonuclear dimers. A comparison of the energy as a function of interatomic distance showed that the simplified energy functional obtains the equilibrium bond length and vibrational frequency almost as well as the self-consistent calculation. The binding energies were found to be in reasonable agreement but larger (note that

the Harris functional can give a total energy which is lower than the self-consistent value, as opposed to any scheme based on the standard energy functional). In a previous paper⁴ we have presented first applications of the Harris functional to solids. Using the LMTO-ASA method (linear muffin-tin orbitals method in the atomic-sphere approximation) of Andersen,⁸ energy-volume curves were calculated for Be, Al, V, Fe, Si, and NaCl. The results showed that, similar to the case of the dimers, the equilibrium lattice constant and bulk modulus were reproduced well, while the cohesive energy often exhibited overbinding. In the following, we show that the Harris functional can also describe the small energy changes associated with phonons and elastic distortions. As test cases, we have chosen C and Si in the diamond structure. For these, it is well known that phonons and elastic constants calculated within the local-density approximation agree very well with the experimental values.^{9,10} Finally, we consider the energy-volume curves for various crystalline phases of Si.

II. METHOD

A calculation of small distortion energies makes it necessary to evaluate all energy terms to a high degree of precision. We have used a recently developed full-potential (FP) LMTO technique¹⁰ for this purpose. The method expresses potential and charge density as spheric harmonic expansions inside nonoverlapping muffin-tin spheres. In the interstitial region, a convenient form is obtained by fitting an expansion in atom-centered Hankel functions to interpolate smoothly between the values and slopes on the sphere surfaces [we will use the term “Hankel function” to denote functions $H_L(\mathbf{r}) = h_l(\kappa\mathbf{r})Y_L(\hat{\mathbf{r}})$ as well as the radial part alone]. For systems which are reasonably close packed, this leads to an accurate description of the interstitial quantities. The accuracy can be monitored by observing the dependence of the total energy on the kinetic energy (i.e., the localization) of the Hankel functions which are used in the fit. As is usual in the LMTO method, the sphere packing can be improved by including “empty spheres”¹¹ if needed. The fitting techniques makes possible an efficient evaluation of the complicated three-center terms in the Hamiltonian matrix, the output charge density, the various total-energy terms, and the effective potential. The Poisson equation can be solved analytically in the Hankel function representation. The results of self-consistent calculations for phonons, elastic constants, shear splittings, and energy-volume curves agree very well with the experiment, as was shown in Ref. 10 for Si and is shown below for C.

The modifications of the FP-LMTO method which are required for the evaluation of the Harris energy functional are straightforward. As was done in the previous work,⁴ we begin by fitting a series of spherical Hankel functions of angular momentum zero to the free-atom charge density outside radius, which is taken as the muffin-tin radius in the crystal. The fit is essentially exact since as many functions as are needed are included; we have used 4 functions with kinetic energies $-1, -2, -6,$

and -10 Ry. Using standard structure-constant expansions for the Hankel functions⁸ and Ewald summation, it is then easy to calculate the overlapped (nonspherical) charge density inside the muffin-tin spheres. It is expressed as a sum of numerical radial functions times spheric harmonics in each sphere. At this point, the values and slopes of the density and of the exchange-correlation potential and the energy density on the sphere surfaces are known. The interstitial fit yields these quantities as linear combinations of Hankel functions in the interstitial. As in the self-consistent FP-LMTO method, it is then possible to calculate the electrostatic potential, the double-counting energy terms, and the Hamiltonian and overlap matrices for the LMTO basis functions.

The free-atom configuration in our calculations were s^2p^2 . As in Ref. 10, we have used a basis of 22 LMTO's centered on the Si and C atoms, consisting of tripled s and p orbitals and doubled d orbitals. This basis gives absolute convergence to about 1 mRy. The kinetic energies of the LMTO envelopes are not critical and were taken as 0, -1 , and -2.3 Ry. For the diamond, simple-cubic, and β -tin structures, one (respectively two for β -tin) empty sphere per Si atom was included to improve the fitting. Muffin-tin radii were chosen to be almost touching; for diamond-structure Si they were 2.13 a.u. and for diamond-structure C they were 1.40 a.u. at the experimental lattice constant, and scaled when the lattice constant was changed. The energies of the Hankel functions used in the fit were taken at -1 and -3 Ry. Varying these from $-0.5, -1$ to $-3, -10$ leads to changes in the total energy of less than 2 mRy for β -tin and less than 1 mRy in all other cases. The fit functions included the functions with l up to 4. Inside the spheres, terms up to $l=4$ in the charge density and the potential were included by explicit expansion in spherical harmonics, and higher angular momenta were included implicitly as tails of the fit functions. For the \mathbf{k} -space integration, a shifted mesh of 19 "special points"¹² was used for the undistorted diamond structure, and correspondingly more points for reduced symmetries. For the metallic Si phases, a regular mesh of 59, 256, 256, and 286 points was used for β -tin, fcc, bcc, and sc, respectively, and a Gaussian broadening of 20 mRy. The self-consistent calculations for C were done in the same way as those for Si described in Ref. 10.

III. RESULTS

In Table I we compare experimental and calculated values for various quantities for Si and C in the diamond structure. As expected, the self-consistent values for lattice constant and bulk modulus reproduce the experiment closely, while the cohesive energy is too large. The new feature is that the Harris energy functional yields results for elastic constants and phonons which are almost as precise as those of the self-consistent calculation. This is surprising, since the overlapped free-atom trial density deviates strongly from the self-consistent density in the bond, as is shown in Fig. 1. Specifically, any density obtained by superimposing spherical atom-centered densities must give zero for the "forbidden" (222) Fourier coefficient which is associated with the buildup of bond

charge. Additional defects of the trial density are that it is too high by a factor of 1.8 in the interstitial, and it does not rise as steeply as one approaches the atoms. Nevertheless, the bond-stretching and bond-bending forces which determine the phonon frequencies are clearly well described. This includes the subtle effects which lead to the soft TA(X) mode. We conclude that the Harris energy functional is suitable for the calculation of distortion energies in solids in addition to the lattice constant and bulk modulus considered previously.

The one quantity for which the Harris-energy functional gives a somewhat larger error is the cohesive energy. The total energy is lower than the self-consistent energy by 6.6 mRy/atom for Si and 26.0 mRy/atom for C. This is consistent with previous calculations for dimers and solids and reflects that the Harris energy functional is variational but not minimal at the self-consistent density. To investigate the question of the "vertical" position of the energies more closely, we have calculated the well-known⁹ energy-volume curves for a number of existing and hypothetical structures of Si. The results of the Harris energy-functional scheme are compared to the self-consistent FP-LMTO calculations in Fig. 2(a). The deviation is at most 2 mRy/atom for the metallic phases and about 7 mRy/atom in the diamond phase. Also, the minimum of the curves are shifted to smaller volumes by the Harris energy functional. However, overall the energy-volume curves are quite acceptable.

The problem of the agreement between the Harris and self-consistent energies can best be discussed by comparing the trial density with the true self-consistent density. Two questions are relevant here. First, one would like to know in what sense the trial density must be correct to obtain an accurate energy value; it is conceivable that the energy functional responds much more sensitively to some types of density deviations than others. Secondly, it is of interest whether some simple prescription for modifying the trial density can be found which further improves the calculated energies.

For the case of Si in the diamond structure it was noted before that the overlapped free-atom charge density compared to the self-consistent charge density (a) is too low in the bond, (b) is too high in the interstitial, and (c) rises less steeply close to the atoms. Some or all of these points could be influenced by changing the localization of the free-atom density. It is clear that a transferable atom-centered density must be spherical. A practical way to modify the free-atom density was recently suggested by Finnis¹³ in the context of pseudopotential calculations. He multiplied the free-atom pseudodensity by a Fermi-factor cutoff of the radius,

$$\frac{1}{\exp[\beta(r - r_c)] + 1}, \quad (5)$$

and then renormalized it. The position of the step (r_c) and the width of the step (β) were changed to vary the trial density. Finnis found that the accuracy of the calculated Al(111) surface energy could be improved dramatically by a certain amount of contraction in this way. More specifically he found that this energy has a maximum in the space of the r_c and β , and that the value at

TABLE I. Static and dynamical properties of silicon and carbon in the diamond structure. The second, third, and fourth columns are the results of self-consistent calculations and non-self-consistent Harris calculations using free-atom density with and without contraction, respectively.

	Expt.	FP-LMTO	Harris	Contracted
Si:				
Lattice constant (a_0)	10.26 ^a	10.23	10.14	10.21
Cohesive energy (eV/atom)	4.63 ^a	5.17	5.25	5.17
Bulk modulus (Mbar)	0.98 ^b	0.99	0.99	0.91
$C_{11}-C_{12}$ (Mbar)	1.02 ^b	1.02	1.15	1.08
C_{44} (Mbar)	0.80 ^b	0.83	0.63	0.66
k_{xyz} (eV/ a_0^3)	-35.1 ^b	-39.1	-42.2	-40.2
ζ	0.54 ^c	0.51	0.55	0.54
$\nu_{LTO}(\Gamma)$ (THz)	15.53 ^a	15.47	15.70	15.38
$\nu_{TO}(X)$ (THz)	13.90 ^a	13.75	13.34	13.42
$\nu_{LAO}(X)$ (THz)	12.32 ^a	11.82	12.16	11.94
$\nu_{TA}(X)$ (THz)	4.49 ^a	4.50	4.40	4.23
C:				
Lattice constant (a_0)	6.75 ^a	6.70	6.54	
Cohesive energy (eV/atom)	7.37 ^a	8.77	9.13	
Bulk modulus (Mbar)	4.42 ^a	4.70	5.04	
$C_{11}-C_{12}$ (Mbar)	9.51 ^a	9.56	11.66	
C_{44} (Mbar)	5.77 ^a	5.34	6.06	
$\nu_{LTO}(\Gamma)$ (THz)	39.9 ^a	39.20	41.40	
$\nu_{TO}(X)$ (THz)	32.0 ^a	31.77	31.47	
$\nu_{LAO}(X)$ (THz)	35.5 ^a	35.04	39.90	
$\nu_{TA}(X)$ (THz)	24.2 ^a	23.74	26.03	

^a Landolt-Börnstein: Numerical Data and Functional Relationships: Science, edited by O. Madelung, New Series, Vol. 22a (Springer, New York, 1987).

^bH. J. McSkimin and P. Andreatch, J. Appl. Phys. **35**, 2161 (1964); **35**, 3312 (1965).

^cC. S. G. Cousins, L. Gerward, J. Staun Olsen, B. Selsmark, and B. J. Sheldon, J. Phys. C **20**, 29 (1987).

the maximum was almost equal to the self-consistent one. We have used a similar procedure to adjust the trial density for diamond-structure Si. The free-atom density was separated into a core and a valence part and the valence density was modified as described. By varying the position and broadening of the cutoff over a wide range, we found that the Harris total energy was always below the self-consistent value and that it was maximal for $\beta=2$ a.u.⁻¹ and $r_c=4.5$ a.u. The Harris and self-consistent energies then agree very well to within 0.4 mRy/atom.

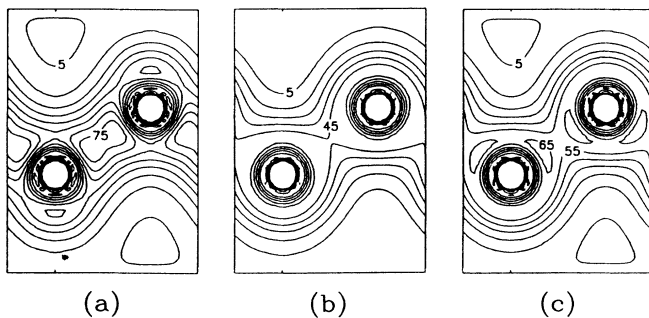


FIG. 1. Comparison of (a) self-consistent, (b) overlapped free-atom, and (c) overlapped contracted free-atom charge densities for diamond-structure Si in the (110) plane. The contour unit is 0.001 electrons/(a.u.)³, the spacing is 0.01 electron/(a.u.)³.

In Fig. 2(b) we show the energy-volume curves obtained using this contracted density in the Harris energy functional. Just as in the free-atom case, the spherical density which was overlapped was the same for all structure and volumes. Figure 2 shows that the contraction has im-

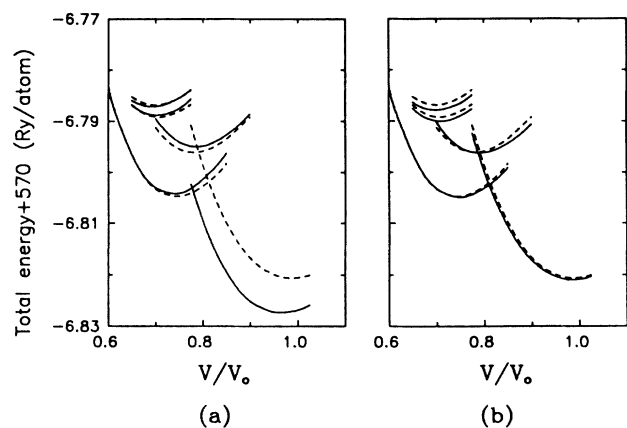


FIG. 2. Comparison of Harris-functional energy-volume curves (solid lines) with the self-consistent result for various phases of Si. (a) Total energies obtained from the free-atom s^2p^2 density; (b) from the contracted density, as described in the text. The crystal structures in sequence of increasing energy are diamond, β -tin, simple-cubic, bcc, and fcc.

proved not only the diamond-structure curve, but also the β -tin and the SC energies. In addition, the minimum of the diamond-structure energy has been moved much closer to the self-consistent result. This shows that the optimization for one case gives a prescription for modifying the trial density which is transferrable to other structures and volumes. From the density plots one can deduce that the true self-consistent density contracts when the free atoms form the crystal. This can be understood as the occupation of bonding states, which lie lower in energy and are more localized than the free-atom orbitals. It is interesting that Weinert and Watson¹⁴ also found it necessary to contract the free-atom densities in order to obtain accurate values for the work function of metals from a similar potential construction as we have used. We have also recalculated the elastic constants and phonon frequencies using the contracted density (column four of Table I). For these quantities there is very little change when the optimized trial density is used. Since the distortions were calculated at the theoretical equilibrium lattice constant, the main effect is some softening of the force constants due to the slightly larger lattice constant.

The modification of the trial density which leads to elimination of 92% of the total-energy error should be visible in the trial density itself. Figure 1(c) shows the diamond-structure Si charge density which results if the contracted density is overlapped at the experimental lattice constant. Comparison of the three densities shows that the trial density in the bond region is still very different from the self-consistent density. On the other hand, the densities in the interstitial now agree almost exactly. The optimization of the trial density has minimized the error for those features to which the Harris energy functional reacts most sensitively. In a Fourier representation, it is the lowest nonconstant component [that is, the (111) component] which moves charge from the Si atoms to the interstitial sites. The details of the charge distribution in the bond are governed by Fourier components which are associated with longer reciprocal vectors. Thus, it seems that for a "good" trial density it is most important that the long-wavelength (i.e., short-reciprocal-vector) components are correct. It has been shown³ that to second order the error in the Harris total energy is given by

$$E_H[n_{in}] - E[n_{sc}] = \frac{1}{2} \int \int \frac{\delta^2 E}{\delta n^2} \Big|_{n=n_{sc}} \Delta n_{in} \Delta n_{out}, \quad (6)$$

where Δn_{in} and Δn_{out} are the errors in the input (trial) and output densities, respectively. To obtain n_{out} from n_{in} , the Poisson equation and the Schrödinger equation are both solved once. Since these are smoothing operations, Δn_{out} is small if Δn_{in} contains only short-wavelength components. Long-wavelength errors in the trial density lead to a large Δn_{out} and consequently to a larger total-energy error. These points should be useful when constructing Harris trial densities in other applications.

The results have shown that whereas it seems unprob-

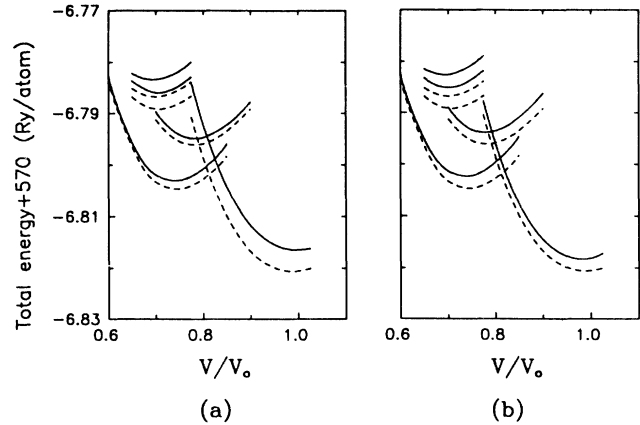


FIG. 3. Comparison of E_{KS1} , energy-volume curves (solid lines) with the self-consistent result for various phases of Si. (a) Total energies obtained from the free-atom s^2p^2 density; (b) from the contracted density, as described in the text. The crystal structures in sequence of increasing energy are diamond, β -tin, simple-cubic, bcc and fcc.

lematic to calculate the elastic constants and phonon frequencies with "one-shot" total-energy techniques, it is more difficult to obtain the energy-volume curves correctly. Therefore we have also calculated these using the functional E_{KS1} , that is, the total energy after the first iteration of the self-consistency cycle. Figure 3(a) shows the curves obtained from the free-atom Si density in this way. While the size of the deviations from the self-consistent result are similar to those of the Harris energy functional, the relative positions are more accurate. All approximate energies from E_{KS1} lie above the self-consistent energies and the net effect is similar to a rigid

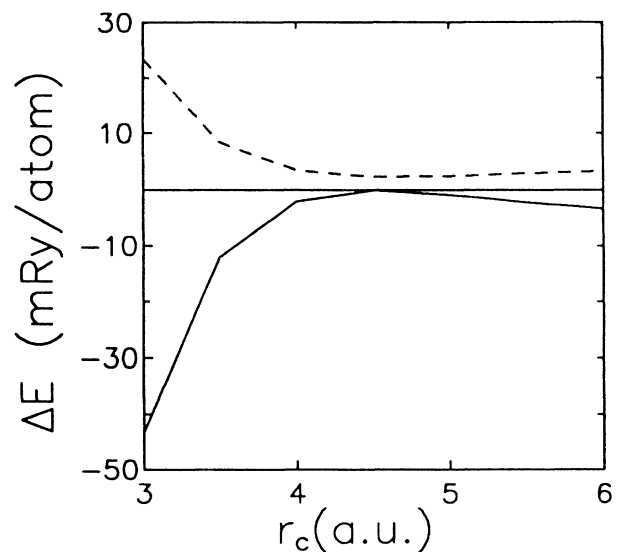


FIG. 4. Deviation of the Harris total energy (solid line) and the E_{KS1} energy (dashed line) from the self-consistent energy (horizontal line) for diamond-structure Si at the experimental volume and $\beta=2.0$ a.u.⁻¹ as a function of r_c .

vertical shift by 2 to 3 mRy. Using the same prescription for contracting the atomic density as before, we have minimized E_{KSI} in the two-parameter space. It turned out that the optimal density is almost the same as that which was determined for the Harris energy functional E_H . In Fig. 4, the variation of the energy with r_c at fixed $\beta=2.0 \text{ a.u.}^{-1}$ is displayed. The optimization is much more successful for E_H than E_{KSI} . A possible explanation is that the deviation of the density in the bond (which cannot be eliminated as long as spherical densities are overlapped) is more significant for E_{KSI} than E_H . The energy-volume curves using the contracted density in E_{KSI} are shown in Fig. 3(b). While the diamond-structure Si curve is improved somewhat, the errors in the metallic phases become larger. Overall, the best description is obtained by using the contracted density in the Harris energy functional. From the present calculations, the main conclusion is that the two functionals react differently to errors in the trial density. Further calculations are needed to determine which prescription is more suitable for more complicated systems and larger unit cells.

IV. SUMMARY AND CONCLUSIONS

The total energy of the Harris functional is obtained by overlapping free-atom charge densities to make a crystal trial density, calculating the effective potential, and solving the Schrödinger equation once. We have calculated cohesive properties, phonon frequencies at points Γ and X , and elastic constants for Si and C in the diamond structure in this way and have compared them to the fully self-consistent results. The quantities calculated with this approximate (and much more efficient) scheme agree

with the experimental values almost as well, but can be obtained without the effort of self-consistency iterations. Additional calculations for Si in various metallic phases showed that the energy-volume curves for Si are also reproduced with reasonable accuracy. However, over-binding by 6.6 mRy/atom in the diamond-structure phase was found. It was possible to improve the agreement to the self-consistent energy-volume curves considerably by using a contracted free-atom density to construct the trial charge density. The optimal contracted density was determined by maximizing the Harris total energy for the diamond structure at the experimental lattice constant as a function of two parameters. Inspection of the improved diamond-structure Si trial density showed that the density in the interstitial region is corrected, while the bond region is not well described by either trial density. The contraction has only an insignificant effect on the phonon frequencies. The global improvement of the energy-volume curves by the contraction indicates that the modified construction of the trial density can be transferred between structures. Comparison to an alternative scheme (evaluation of the energy after the first iteration) showed that both schemes give errors of similar magnitude. In conclusion, our results indicate that non-self-consistent techniques could be useful in the future to obtain accurate total energies for large and complicated systems which are difficult to treat with the conventional self-consistent approach.

ACKNOWLEDGMENTS

The authors would like to thank O. K. Andersen for proposing this project to them and for useful guidance, and M. Scheffler and M. Finnis for helpful discussions.

*Permanent address: Department of Physics, Aristotle University of Thessaloniki, GR-54006 Thessaloniki, Greece.

†Present address: Fritz-Haber-Institut, Faradayweg 4-6, D-1000 Berlin 33, Federal Republic of Germany.

¹P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

²J. Harris, Phys. Rev. B **31**, 1770 (1985).

³W. M. C. Foulkes, Ph.D. thesis, University of Cambridge, 1987; W. M. C. Foulkes and R. Haydock, Phys. Rev. B **39**, 12 520 (1989).

⁴H. M. Polatoglou and M. Methfessel, Phys. Rev. B **37**, 10 403 (1988).

⁵J. R. Chelikowski and S. G. Louie, Phys. Rev. B **29**, 3470 (1984).

⁶O. K. Andersen, M. Methfessel, C. O. Rodriguez, P. Blöchl, and H. M. Polatoglou, *Atomistic Modeling of Materials: Beyond Pair Potentials* (Plenum, New York, 1989); H. M. Po-

latoglou and M. Methfessel, Fourth International Workshop on Computational Condensed-Matter Physics: Total Energy and Force Methods, Trieste, 1989 (unpublished).

⁷A. J. Read and R. J. Needs, J. Phys. Condens. Matter **1**, 7565 (1989).

⁸O. K. Andersen, Phys. Rev. B **12**, 3060 (1975); H. L. Skriver, in *The LMTO Method* (Springer, New York, 1984).

⁹M. L. Cohen, in *Highlights of Condensed-Matter Theory*, edited by F. Bassani, F. Fumi, and M. P. Tosi (North-Holland, New York, 1985), p. 16.

¹⁰M. Methfessel, Phys. Rev. B **38**, 1537 (1988); M. Methfessel, C. O. Rodriguez, and O. K. Andersen, *ibid.* **40**, 2009 (1989).

¹¹D. Glötzel, B. Segall, and O. K. Andersen, Solid State Commun. **36**, 403 (1980).

¹²D. J. Chadi and M. L. Cohen, Phys. Rev. B **8**, 5747 (1973).

¹³M. W. Finnis, J. Phys. Condens. Matter **2**, 331 (1990).

¹⁴M. Weinert and R. E. Watson, Phys. Rev. B **29**, 3001 (1984).