

## Validity of the frozen-core approximation and pseudopotential theory for cohesive energy calculations

U. von Barth

*Department of Theoretical Physics, University of Lund, Lund, Sweden*

C. D. Gelatt\*

*Physics Department, Harvard University, Cambridge, Massachusetts 02138*

(Received 8 January 1979)

When atoms are brought together to form molecules or solids the change in the kinetic energy of the core electrons can be an order of magnitude larger than the change in total energy. In spite of this, pseudopotential methods, which neglect the redistribution of the core electrons, give results very close to the fully self-consistent results. We explain this apparent contradiction by showing that the correction to the frozen-core approximation, an approximation used implicitly in a pseudopotential calculation, vanishes to first order in the charge-density differences and we give a closed formula for the second-order correction. The cancellation of large errors involved in the frozen-core approximation is demonstrated for valence-electron configuration changes in several free atoms and for a bcc to fcc transformation of Mo. In all cases the frozen-core approximation makes an error of less than 5% in the energy of transformation, and the second-order correction formula accurately reproduces this error.

### I. INTRODUCTION

Within the past year several groups have proposed pseudopotentials to be used in the calculation of the electronic structure<sup>1</sup> and binding properties<sup>2</sup> of transition metals. Pseudopotential methods<sup>3</sup> have the conceptual advantage of concentrating on the electronic states that one expects to be involved in bonding, but the validity of the frozen-core approximation used implicitly in the pseudopotential methods has been challenged<sup>4</sup> by recent fully self-consistent calculations.

Such calculations<sup>4,5,6</sup> have demonstrated that the core wave functions are not insensitive to the atomic environment. For example, the kinetic energy of the core states of Mo increases by 5 eV when the crystal is formed, while the change in total energy is 6.7 eV per atom.<sup>7</sup> Similarly, if one calculates the total energy difference between bcc and fcc Mo, one finds a transformation energy of 0.5 eV per atom and a core kinetic-energy change of 2.7 eV. Similar results indicating large core kinetic-energy changes (and thus significant changes in the shape of core orbitals) accompanying structure changes were obtained by Janak<sup>4</sup> for nearly-free-electron metals.

The facts would seem to invalidate pseudopotential methods for calculating the binding properties of metals. In these methods one constructs an effective Hamiltonian for the valence electrons that incorporates the effect of the core electrons. The core part of the pseudo-Hamiltonian is considered to be a fixed quantity, independent of the surroundings of the atom<sup>8</sup> and unchanged when the pseudopotential calculation is iterated to valence self-

consistency.<sup>9</sup> This concept of transferability relies on the assumption that the core-electron wave functions are not affected by different environments, an assumption that the fully self-consistent calculations indicate is unjustified.

The present paper will explain the quantitative success of pseudopotential calculations of binding properties<sup>2,8</sup> by showing that the magnitude of the errors in total energies and orbital binding energies associated with the frozen-core approximation are quite small, even though errors in individual components of the total energy can be large. This will be done by deriving an expression, within local-density theory,<sup>10</sup> for the frozen-core-approximation error defined as the total-energy difference between a fully self-consistent calculation and a calculation in which the core-electron density is kept fixed at its value for a fully self-consistent calculation in a different environment (one might use the frozen-atomic-core electron density in a solid-state calculation, for example). In the frozen-core calculation only the valence-charge density is allowed to respond to the different environment and is treated self-consistently. The error expression demonstrates that to *first order* in the charge-density differences the frozen-core approximation for the total energy is *exact*. An explicit formula is derived for the nonvanishing second-order contributions. These formal results indicate that while nonvariational components of the energy such as the kinetic energy may be quite sensitive to the frozen-core approximation, the total energy, which is variational in the charge density, is not.

We have tested our error expression on two

classes of environmental changes that are known to cause significant changes in the shape of the more loosely bound core orbitals. The first class is a change in atomic-valence-electron configuration in elements for which some of the valence orbitals have the same principal quantum number as core orbitals. One finds such changes, for example, when comparing the valence-electron configuration of the transition-metal atoms with the valence configuration in the solid.<sup>11</sup> The accompanying change in total energy is a significant component in the cohesive energy.<sup>12</sup> Since the transition-metal  $d$  orbital has the same principal quantum number as the least tightly bound core orbitals, changes in  $d$  configuration will change the screening of these orbitals and thus affect their shape and their kinetic energy. We have calculated the frozen-core-approximation error for valence  $d$  to  $s$  interconversion for Ca, Sc, Cu, and Mo atoms. The error is typically only a few percent of the configuration-change energy, and thus less than 0.1 eV per atom for the magnitude of configuration changes appropriate to the change from the atomic to the solid-state environment.

The second class of examples is the calculation of the energy cost of a crystal-structure change. We have calculated this structural-energy difference for bcc and fcc Mo using the fully self-consistent augmented-spherical-wave method<sup>5</sup> and compared the result with a calculation for the fcc structure using the frozen core from the bcc calculation. Consistent with the theoretical analysis, we find that the error made in the frozen-core calculation is less than two percent of the structural-energy difference.

We conclude that pseudopotential methods based on the frozen-core approximation are sufficiently accurate, on the scale of precision of present calculations of total energies, to be used for the analysis of bonding and structure.

In Sec. II we derive the expression for the error in the frozen-core approximation and show that it is of second order in the charge-density differences. An approximation to the exact second-order result is developed that can be calculated without resorting to a fully self-consistent calculation. In Sec. III we discuss our numerical results and show the compensating kinetic- and potential-energy changes that lead to the vanishing of the first-order term in the frozen-core error. In addition, we discuss errors in orbital eigenvalues. Section IV is a discussion of our conclusions.

## II. FROZEN-CORE TOTAL-ENERGY ERROR

In the density-functional theory by Hohenberg, Kohn, and Sham<sup>10</sup> the total energy is a functional,

$E\{\rho, w\}$ , of the electronic charge density  $\rho(\vec{r})$  and the external potential  $w(\vec{r})$ . The physical charge density for a given  $w$  is the one that minimizes the energy functional with the constraint of particle conservation. In the local-density version of the theory<sup>10</sup> the functional is given by

$$E\{\rho, w\} = T_0\{\rho\} + \frac{1}{2} \iint \rho v \rho + \int \rho w + \int \rho \epsilon_{xc}(\rho), \quad (1)$$

where  $T_0\{\rho\}$  is the kinetic energy of noninteracting electrons having density  $\rho(\vec{r})$ ,  $\epsilon_{xc}(\rho)$  is the exchange-correlation energy per particle of the homogeneous electron gas of density  $\rho$ , and  $v(\vec{r})$  is the Coulomb interaction. We have here and throughout the paper adopted a notation in which spatial variables and integration symbols such as  $d^3r$  are suppressed.

In the present work we are interested in frozen-core calculations, i.e., calculations in which only the valence charge is allowed to vary. It would then be convenient to have a generalization of the exact total-energy functional that would be a functional of the core and valence charges ( $\rho_c$  and  $\rho_v$ ) separately. Since the accuracy of the frozen-core approximation certainly depends very little on the specific approximation chosen for the exchange-correlation energy, it will be sufficient for our purposes to generalize the local-density approximation (1) rather than the full density-functional theory. The last three terms of Eq. (1) are trivially generalized by replacing  $\rho$  by  $\rho_c + \rho_v$ . In order to show that the kinetic energy of noninteracting electrons also can be considered as a functional of their core and valence charges separately, we have to consider the response of noninteracting electrons to a composite external potential ( $w_c, w_v$ ) where  $w_c$  is to be used only for core orbitals and  $w_v$  only for valence orbitals. This means that we will treat the core and the valence electrons as two different kinds of particles and consequently orthogonality between core and valence orbitals should not be expected. This non-orthogonality is, however, inherent in all frozen-core calculations. It should be stressed that the procedure is a purely mathematical trick to estimate the frozen-core error. The resulting functional  $T_0\{\rho_c, \rho_v\}$  will certainly be different from the functional  $T_0\{\rho_c + \rho_v\}$ .

It is not difficult to see that the original arguments of Hohenberg and Kohn can be used to demonstrate the functional dependence on the core-charge density, but this technique can not be used to show the functional dependence on the valence-charge density. Instead we use response theory and consider small deviations of the potentials  $w_c$  and  $w_v$  from the physical potential  $w$ . If the valence potential  $w_v$  changes from  $w$  to  $w + \delta w_v$ , per-

turbation theory carried to second order gives a change  $\delta T_0$  in the kinetic energy,

$$\delta T_0 = - \int w \delta \rho_v - \frac{1}{2} \int \delta w_v P_v \delta w_v + O((\delta w_v)^3). \quad (2)$$

Here

$$\delta \rho_v = \int P_v \delta w_v + O((\delta w_v)^2), \quad (3)$$

where  $P_v$  is the polarizability of noninteracting valence electrons in the potential  $w$ . The first term in Eq. (2) is obviously a functional of  $\rho_v$  but, given  $\delta \rho_v$ , Eq. (3) only determines  $\delta w_v$  to within a potential  $u$  satisfying  $P_v u = 0$ . This ambiguity does not however affect the second term in Eq. (2). Consequently,  $T_0$  is a functional of  $\rho_v$  locally, to second order, around the physical valence density.<sup>13</sup>

The functional dependence of  $T_0$  on the core-charge density  $\rho_c$  is proven similarly, and we note that the change in the kinetic energy due to a simultaneous change  $(\delta w_c, \delta w_v)$  in both the core and the valence potentials is given by a sum of two terms of the form (2), one containing  $\delta \rho_v$ ,  $\delta w_v$ , and  $P_v$  and the other  $\delta \rho_c$ ,  $\delta w_c$ , and  $P_c$ . This additivity of the changes in our new functional  $T_0\{\rho_c, \rho_v\}$  implies that

$$\frac{\delta T_0^2}{\delta \rho_c \delta \rho_v} = 0, \quad (4)$$

a fact that will prove important later on. We also note that when  $w_c = w_v = w$ ,  $T_0\{\rho_c, \rho_v\}$  will reduce to  $T_0\{\rho_c + \rho_v\}$  i.e., to the value of the usual noninteracting kinetic-energy functional defined by Hohenberg and Kohn.

We complete our generalization of the functional  $E\{\rho, w\}$  to a functional  $E\{\rho_c, \rho_v, w\}$  of core and valence charge by replacing  $T_0\{\rho\}$  by  $T_0\{\rho_c, \rho_v\}$  in Eq. (1) and by noting that

$$\begin{aligned} \rho(\vec{r}) &= \rho_c(\vec{r}) + \rho_v(\vec{r}), \\ \rho_c(\vec{r}) &= \sum_{i \in \text{core}}^{\text{occ}} |\psi_i(\vec{r})|^2, \\ \rho_v(\vec{r}) &= \sum_{i \in \text{valence}}^{\text{occ}} |\psi_i(\vec{r})|^2. \end{aligned} \quad (5)$$

The definition of a core state and a valence state is of course arbitrary to some extent but in practice it is not hard to make a choice.<sup>14</sup>

Define three separate calculations for a system:

(i) A reference calculation used to define the core-charge density to be used in a frozen-core calculation for a different chemical environment. Quantities for this calculation will be denoted by a zero superscript.

(ii) The frozen-core calculation itself. Results of this calculation will be denoted by an asterisk.

(iii) The fully self-consistent calculation in the

same environment as the frozen-core calculation. These results are not superscripted.

Thus let  $\rho_c$  and  $\rho_v$  be the fully self-consistent core- and valence-charge densities for a solid or a molecule and let  $w$  be the corresponding external potential. For a molecule or solid where all atoms are the same  $w(\vec{r})$  would be  $-Z \sum_{\vec{R}} v(\vec{r} - \vec{R})$  where  $Z$  is the atomic number,  $v$  is the Coulomb potential, and the  $\vec{R}$ 's are the atomic positions. The core-charge density that defines our frozen-core approximation is  $\rho_c^0$ , and  $\rho_v^*$  is the valence-charge density which is self-consistent in the field of the fixed core-charge density  $\rho_c^0$  and in the external field  $w$ .  $\rho_c^0$  could, e.g., be a superposition of atomic-core-charge densities or the core-charge density from a renormalized atom calculation. Naturally, the closer  $\rho_c^0$  is to  $\rho_c$  the closer  $\rho_v^*$  will be to  $\rho_v$  and the smaller the error in the frozen-core approximation. The error  $\delta$  is now easily written

$$\delta = E\{\rho_c^0, \rho_v^*, w\} - E\{\rho_c, \rho_v, w\}. \quad (6)$$

An expansion of  $\delta$  around the fully self-consistent result gives to second order in the density differences

$$\begin{aligned} \delta &= \int \frac{\delta E}{\delta \rho_c} (\rho_c^0 - \rho_c) + \int \frac{\delta E}{\delta \rho_v} (\rho_v^* - \rho_v) \\ &+ \frac{1}{2} \iint (\rho_c^0 - \rho_c) \frac{\delta^2 E}{\delta \rho_c \delta \rho_c} (\rho_c^0 - \rho_c) \\ &+ \iint (\rho_c^0 - \rho_c) \frac{\delta^2 E}{\delta \rho_c \delta \rho_v} (\rho_v^* - \rho_v) \\ &+ \frac{1}{2} \iint (\rho_v^* - \rho_v) \frac{\delta^2 E}{\delta \rho_v \delta \rho_v} (\rho_v^* - \rho_v). \end{aligned} \quad (7)$$

In the fully self-consistent calculation the energy functional  $E\{\rho_c, \rho_v, w\}$  is stationary with respect to variations in the core- and valence-charge densities separately, and therefore

$$\frac{\delta E\{\rho_c, \rho_v, w\}}{\delta \rho_c(\vec{r})} = \mu_c, \quad \frac{\delta E\{\rho_c, \rho_v, w\}}{\delta \rho_v(\vec{r})} = \mu_v, \quad (8)$$

where  $\mu_c$  and  $\mu_v$  are the Lagrangian multipliers associated with the conservation of core and valence charge. Since the total number of core electrons and the total number of valence electrons are the same for the frozen-core and the self-consistent calculations, the first-order terms in Eq. (7) vanishes. This is the crucial result for the accuracy of the frozen-core approximation.

In order to estimate the magnitude of the second-order terms we need the three second-order derivatives. If we replace  $T_0\{\rho\}$  by  $T_0\{\rho_c, \rho_v\}$ , and  $\rho$  by  $\rho_c + \rho_v$  in Eq. (1), we get an explicit expression for the functional  $E\{\rho_c, \rho_v, w\}$ . From this expression and from the above-mentioned relation

$\delta^2 T_0 / \delta \rho_c \delta \rho_v = 0$ , we infer that

$$\frac{\delta^2 E\{\rho_c, \rho_v, w\}}{\delta \rho_c(\bar{\mathbf{r}}) \delta \rho_v(\bar{\mathbf{r}}')} = v(\bar{\mathbf{r}} - \bar{\mathbf{r}}') + \mu'_{xc} \delta(\bar{\mathbf{r}} - \bar{\mathbf{r}}'). \quad (9)$$

Here  $\mu'_{xc}$  is the density derivative, evaluated at the total density  $\rho(\bar{\mathbf{r}})$ , of the exchange-correlation contribution to the chemical potential of the homogeneous electron gas. The derivatives  $\delta^2 E / \delta \rho_c^2$  and  $\delta^2 E / \delta \rho_v^2$  are more complicated since the kinetic-energy parts of these derivatives are not easily obtainable. In order to circumvent this difficulty we make use of the fact that the density  $\rho_v^*$  is the valence-charge density that minimizes the energy in the frozen-core calculation. This implies that

$$\frac{\delta E\{\rho_c^0, \rho_v^*, w\}}{\delta \rho_v(\bar{\mathbf{r}})} = \mu_v^*. \quad (10)$$

Expanding this first derivative around the self-consistent solution  $\{\rho_c, \rho_v, w\}$ , multiplying by  $\rho_v^* - \rho_v$ , and integrating gives

$$\iint (\rho_c^0 - \rho_c) \frac{\delta^2 E}{\delta \rho_c \delta \rho_v} (\rho_v^* - \rho_v) + \iint (\rho_v^* - \rho_v) \frac{\delta^2 E}{\delta \rho_v \delta \rho_v} (\rho_v^* - \rho_v) = 0, \quad (11)$$

which when substituted into Eq. (7) relieves us from having to evaluate  $\delta^2 E / \delta \rho_c^2$ .

Similarly we would like to be able to evaluate the third term in Eq. (7) from the fact that  $\rho_c^0$  is the self-consistent core-charge density of some reference problem. Usually the free atom is chosen as the reference problem and  $\rho_c^0$  is then a superposition of atomic core densities. It is, however, very difficult<sup>15</sup> to define the energy functional that is minimized by this choice of  $\rho_c^0$ . The effective potential that gives rise to  $\rho_c^0$  is certainly not a superposition of atomic potentials and the problem becomes even harder if the cores overlap. To overcome this difficulty we will simply say that  $\rho_c^0$  is the self-consistent charge density of core electrons moving in some suitably chosen but fixed valence charge  $\rho_v^0$  and in some external potential  $w^0$ . By choosing  $\rho_v^0$  and  $w^0$  properly we could of course make  $\rho_c^0$  very close to a superposition of atomic-core-charge densities. We could also simulate the core-charge density of a renormalized atom calculation. The external potential  $w^0$  would always include the potentials from nuclei with the same charges and positions as  $w$  but would also include nonsingular and slowly varying parts with the full symmetry of the system under consideration. These features allow us to use first-order perturbation theory for the difference

potential  $w^0 - w$ .

Thus from the definition of our frozen core  $\rho_c^0$  we have

$$\frac{\delta E\{\rho_c^0, \rho_v^0, w^0\}}{\delta \rho_c(\bar{\mathbf{r}})} = \mu_c^0, \quad (12)$$

with some constant  $\mu_c^0$  independent of  $\bar{\mathbf{r}}$ . Again expanding this first derivative around the fully self-consistent solution, multiplying by  $(\rho_c^0 - \rho_c)$ , and integrating gives

$$\iint (\rho_c^0 - \rho_c) \frac{\delta^2 E}{\delta \rho_c \delta \rho_c} (\rho_c^0 - \rho_c) + \iint (\rho_c^0 - \rho_c) \frac{\delta^2 E}{\delta \rho_c \delta \rho_v} (\rho_v^0 - \rho_v) + \iint (\rho_c^0 - \rho_c) \frac{\delta^2 E}{\delta \rho_c \delta w} (w^0 - w) = 0. \quad (13)$$

It follows from the expression for the energy functional [Eq. (1)] that  $\delta^2 E / \delta \rho_c \delta w = 1$ . Substituting the results of Eqs. (11) and (13) into Eq. (7), we obtain the explicit second-order formula for the frozen-core error,

$$\delta = \frac{1}{2} \iint (\rho_c^0 - \rho_c) \frac{\delta^2 E}{\delta \rho_c \delta \rho_v} (\rho_v^* - \rho_v^0) + \frac{1}{2} \int (\rho_c^0 - \rho_c)(w - w^0). \quad (14)$$

The effective one-particle potentials for the frozen-core calculation and for the reference problem are

$$V^*(\bar{\mathbf{r}}) = w + \int \rho^* v + \mu_{xc}(\rho^*) \quad (15)$$

and

$$V^0(\bar{\mathbf{r}}) = w^0 + \int \rho^0 v + \mu_{xc}(\rho^0),$$

respectively. Here  $\rho^* = \rho_c^0 + \rho_v^*$  and  $\rho^0 = \rho_c^0 + \rho_v^0$ . Using our explicit expression for  $\delta^2 E / \delta \rho_c \delta \rho_v$ , Eq. (9), we can rearrange Eq. (14) so that our final result for the error  $\delta$  of the frozen-core approximation becomes

$$\delta = \frac{1}{2} \int (\rho_c^0 - \rho_c)(V^* - V^0). \quad (16)$$

This formula clearly exhibits the second-order nature of the corrections. We have also used it to estimate the third- and higher-order effects. In the test cases we have considered (Sec. III) and for which we have calculated the total error due to the frozen-core approximation, we have found that Eq. (16) accounts for more than 95% of the total error, and therefore higher-order effects are negligible.

The expression for the error [Eq. (16)] cannot be used to estimate the error in the frozen-core

approximation if only a frozen-core calculation has been done, since it involves the fully self-consistent core-charge density  $\rho_c$ . An accurate estimate  $\delta^*$  of  $\delta$  can, however, be obtained by allowing the core to relax in the frozen-core potential  $V^*$ , and using the resulting core-charge density  $\rho_c^*$  instead of  $\rho_c$  in Eq. (13). Thus

$$\delta^* = \frac{1}{2} \int (\rho_c^0 - \rho_c^*)(V^* - V^0). \quad (17)$$

This calculation represents the first step towards self-consistency. The next steps would be to let the valence charge relax and then let the core relax again. The difference between  $\delta$  and  $\delta^*$  will be second order in the core polarizability and therefore extremely small. In the Sc test case we found that the difference between  $\delta$  and  $\delta^*$  is of the order of a few percent.

### III. NUMERICAL TESTS OF THE ANALYSIS

When atoms are brought together to form molecules or solids, there will be a redistribution of valence charge which, in turn, will cause a change in the core-charge density. In a solid the valence charge will be compressed: The same number of valence electrons will occupy a smaller region of space in the solid than in the free atom. Also the configuration of the valence electrons will change: The decomposition of the valence charge into different angular momentum components around each nucleus will be different in the solid or in the molecule than in the atom. The compression and the configurational change are the two major changes in the valence density but of these the configurational change has the largest effect on the core-charge density.<sup>7</sup> The energy associated with the configurational change will also be a large part of the cohesive energy.<sup>12</sup> We have therefore tested the frozen-core approximation by applying it to a configurational change in a number of metal atoms (Ca, Sc, Cu, and Mo) and comparing the results to fully self-consistent results for the same change. We have chosen to study these metals because the  $nd$  ( $n = 3$  or  $4$ ) valence orbitals occupy

the same region in space as the  $ns$  and  $np$  core orbitals, and consequently one would expect the frozen-core approximation to be less accurate for these materials. To simulate the solid we change the atomic-ground-state configuration<sup>16</sup> from  $3d^n$ ,  $4s^m$  to  $3d^{m+\delta n}$ ,  $4s^{m-\delta n}$ .

The results can be studied in the first four rows of Table I. In order to demonstrate the large cancellations that occur between different contributions to the error in the energy of the frozen-core approximation, we divide the total energy [Eq. (1)] into a core energy, a valence energy, and a core-valence interaction energy. Thus

$$E\{\rho_c, \rho_v, w\} = E_c + E_v + E_{cv},$$

where

$$\begin{aligned} E_c &= T_c + \frac{1}{2} \int \rho_c v \rho_c + \int \rho_c w + \int \rho_c \epsilon_{xc}(\rho_c), \\ E_v &= T_v + \frac{1}{2} \int \rho_v v \rho_v + \int \rho_v w + \int \rho_v \epsilon_{xc}(\rho_v), \quad (18) \\ E_{cv} &= \int \rho_c v \rho_v + \int \rho \epsilon_{xc}(\rho) - \int \rho_c \epsilon_{xc}(\rho_c) \\ &\quad - \int \rho_v \epsilon_{xc}(\rho_v), \end{aligned}$$

and where  $T_c$  is the sum of the kinetic energies of the individual core orbitals<sup>17</sup> and similarly for  $T_v$ . We use a  $\delta$  in front of these quantities to denote the errors in them due to the frozen-core approximation. Although the error  $\Delta E^* - \Delta E$  is less than 0.1 eV in all cases, the redistribution of the core electrons gives rise to large changes in core kinetic energy ( $\delta T_c$ ). Most of this change comes from the shell that is spatially degenerate with the valence electrons, but the contribution from the more tightly bound core shells is still much larger than the total  $s \rightarrow d$  promotion energy. For Sc, for example,  $\delta T_c^M = 19.08$  eV from the  $M$  shell and  $\delta T_c^{K,L} = -2.50$  eV from the deepest core electrons. The large change in the core kinetic energy is, however, canceled by potential energy terms, a change in the valence energy, and a change of the interaction energy between the core

TABLE I. Energy differences ( $\Delta E$ ) for the indicated changes in state, the frozen-core approximation ( $\Delta E^*$ ) to them, and the difference between  $\Delta E$  and  $\Delta E^*$ .  $\delta$  is the second-order perturbation result [Eq. (14)] for this difference. The remaining columns give the components of the frozen-core error which are defined in the text. All energies in eV.

	$\Delta E$	$\Delta E^*$	$\Delta E^* - \Delta E$	$\delta$	$\delta T_c$	$\delta T_v$	$\delta E_c$	$\delta E_v$	$\delta E_{cv}$
Ca( $s^2 \rightarrow d^{0.5}s^{1.5}$ )	0.97	1.01	0.04	0.04	13.06	-1.45	-0.16	4.31	-4.12
Sc( $d^2 s^2 \rightarrow d^{1.6}s^{1.4}$ )	0.74	0.79	0.05	0.05	16.58	-3.30	-0.55	7.79	-7.20
Cu( $d^{10}s \rightarrow d^{9.6}s^{1.4}$ )	0.56	0.57	0.01	0.01	-10.82	3.19	1.96	-5.27	3.31
Mo( $d^5 s \rightarrow d^{4.65}s^{1.35}$ )	0.12	0.12	0.00	0.00	-7.95	1.89	0.41	-4.68	4.27
Mo(bcc $\rightarrow$ fcc)	0.46	0.46	0.00	0.00	2.71	-0.45	-0.13	1.17	-1.03

TABLE II. Valence equivalences before ( $\epsilon^0$ ) and after ( $\epsilon$ ) an  $s$ - $d$  conversion and the frozen-core approximation for the latter ( $\epsilon^*$ ). The configuration changes are the same as in Table I. Energies in eV.

	$\epsilon_s^0$	$\epsilon_s$	$\epsilon_s^*$	$\epsilon_d^0$	$\epsilon_d$	$\epsilon_d^*$
Ca	-3.95	-3.61	-3.62		-1.42	-1.32
Sc	-4.36	-3.92	-3.94	-3.65	-2.24	-2.14
Cu	-4.78	-5.25	-5.24	-5.59	-7.29	-7.32
Mo	-4.13	-4.41	-4.40	-4.27	-4.95	-4.98

and valence electrons.

A simple way to understand how the cancellation works is to first let the core relax in fixed valence charge and then let the valence electrons relax with the core kept fixed. The total error  $\delta$  [Eq. (6)] will then be the sum of the errors due to these two redistributions. Thus

$$\begin{aligned}\delta_c &= E\{\rho_c^0, \rho_v\} - E\{\rho_c, \rho_v\}, \\ \delta_v &= E\{\rho_c^0, \rho_v^*\} - E\{\rho_c^0, \rho_v\}, \\ \delta &= \delta_c + \delta_v.\end{aligned}\quad (19)$$

Since the total energy must be stationary when the core density is varied and the valence density is kept fixed and vice versa, as in Eqs. (8) and (10), both  $\delta_c$  and  $\delta_v$  are small numbers. In fact, for Sc  $\delta_c = 0.052$ ,  $\delta_v = -0.007$ , and therefore  $\delta = 0.045$  eV as in Table I.

Table II contains a comparison of the valence orbital eigenvalues for the three calculations. It clearly shows that the frozen-core approximation for the valence eigenvalues is quite good ( $\sim 0.1$  eV), although not as good as for the total energies. In the case of a configurational change it is easy to get a relation between the errors in the eigenvalues and the error in the total energy. The energy eigenvalues of local density theory are the derivatives of the total energy with respect to the occupation numbers of the corresponding orbitals<sup>18</sup> and therefore

$$\Delta E = \int_0^{\delta n} [\epsilon_d(d^{n+\nu} s^{m-\nu}) - \epsilon_s(d^{n+\nu} s^{m-\nu})] d\nu, \quad (20)$$

where  $\delta n$  is the number of  $s$  electrons that has been promoted to the  $d$  shell. If one subtracts from Eq. (20) the similar result for the frozen-core approximation, one obtains the same kind of relation [Eq. (20)] with  $\Delta E$  replaced by  $\delta$  and  $\epsilon$  replaced by  $\delta\epsilon = \epsilon^* - \epsilon$ . Obviously  $\delta\epsilon = 0$  when  $\nu = 0$ , and if it is assumed that  $\delta\epsilon(\nu)$  varies linearly with  $\nu$  one obtains

$$\delta = \frac{1}{2} \delta n (\delta\epsilon_d - \delta\epsilon_s). \quad (21)$$

For sc  $\delta n = 0.6$  and from Table II  $\delta\epsilon_d = 0.10$  eV,

$\delta\epsilon_s = -0.02$  eV. This gives  $\delta = 0.04$  eV which is rather close to 0.05 eV from Table I. Equation (21) also shows that the error in the total energy is about half the error in the eigenvalues.<sup>19</sup>

The final row of Table I shows the result of the calculation of the total-energy difference between bcc and fcc Mo. The core-charge density from the fully self-consistent calculation<sup>20</sup> for the bcc structure is used in a frozen-core calculation for the fcc structure. The table contains the analysis of the components of the change. As was found by Janak<sup>4</sup> for structural energy differences of simple metals, the core kinetic energy change is significantly larger than the energy difference between the structures. In spite of this, the frozen-core total-energy error is less than 0.01 eV, the limit of our calculational accuracy.

#### IV. CONCLUSIONS

We have studied the accuracy of the frozen-core approximation by comparing it to fully self-consistent results. Our test cases have been promotions of  $s$  electrons to  $d$  electrons in four metal atoms and a structure change of a mid-period transition metal. We believe these to be realistic simulations of the charge redistributions that take place during chemical binding. The results demonstrate that the error in the total energies due to the frozen-core approximation is small ( $\sim 0.1$  eV), in spite of the fact that the relaxation of the core electrons is accompanied by a change in the kinetic energy of the core that can be two orders of magnitude larger than the error in the total energy. Within the local-density formalism we have shown that this is due to the fact that the first-order correction to the frozen-core approximation vanishes. We have also derived an exact expression for the second-order correction and shown that higher-order corrections are negligible. An approximate version of this expression can be used to estimate the error without resorting to fully self-consistent calculations.

Pseudopotential calculations of cohesive properties implicitly rely on the frozen-core approximation and the present analysis shows that this is not a severe limitation even for transition metals. If, however, higher accuracy than 0.1 eV is desired one would have to let the pseudopotential change with the surroundings or one could perhaps include among the valence electrons those core electrons that have the same principal quantum number as the valence electrons.

One note of caution should be added. The frozen-core approximation does not satisfy the virial theorem. Thus techniques<sup>21</sup> for calculating forces or pressures from the virial theorem, rather than

from derivatives of the total energy, should be used with caution in conjunction with frozen cores.<sup>22</sup>

#### ACKNOWLEDGMENTS

We have benefited from discussions with Professor J. Wilkins and Dr. A. R. Williams, Dr. J. Janak, Dr. V. Peuckert, Dr. C-O Almladh, and Professor L. Gårding, and we acknowledge

the support from the Swedish Natural Science Research Council under Grant Nos. F2163-026 and F2163-032. C.D.G. gratefully acknowledges the hospitality of the Department of Theoretical Physics, University of Lund, where this study was begun. We also acknowledge support from the National Science Foundation under Grant Nos. DMR 76-01111 and DMR 77-10210.

\*Present address: IBM T. J. Watson Research Center, P. O. Box 218, Yorktown Heights, N. Y. 10598.

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<sup>11</sup>For example, transition-metal free atoms typically have a valence configuration  $d^{N-2} s^2$  where  $N$  is the total number of valence electrons. The solid-state configuration for  $3 \leq N \leq 11$  is  $d^{N-x} (sp)^x$  with  $x \approx 1.4$ . A table of such self-consistent solid-state valence configurations for  $3d$  transition metals can be found in A. R. Williams and N. D. Lang, *Phys. Rev. Lett.* **40**, 954 (1978).

<sup>12</sup>This is the "atomic preparation" term in Fig. 4 of C. D. Gelatt, Jr., H. Ehrenreich, and R. E. Watson, *Phys. Rev. B* **15**, 1613 (1977).

<sup>13</sup>It is an interesting side issue that the above technique can easily be adopted to prove the original theorem by Hohenberg and Kohn. Such a proof would relieve one from having to assume that any density can be realized by some external potential. The drawback would be that one would only have a local functional dependence, but such a weaker theorem is all that is needed in practice.

<sup>14</sup>One could, for example, define the core states to be

those states in a solid that have a bandwidth less than 0.1 eV, the remaining occupied states would be valence states. In the  $3d$  series the  $1s$ ,  $2s$ ,  $2p$ ,  $3s$ , and  $3p$  states would be core states, whereas the  $3d$  and the  $4s$  would be valence states.

<sup>15</sup>Note that if the cores overlap, the kinetic energy associated with  $\rho_0^0$  will not be simply the sum of the atomic core kinetic energies as is often assumed.

<sup>16</sup>The solid-state configurations for Ca, Sc, and Cu are from Ref. 11. The Mo configuration is taken from an ordinary self-consistent band-structure calculation for the bcc solid. The solid-state valence configuration should also include states of  $p$  character. The choice of putting all of the non- $d$  electrons into the more contracted  $s$  orbitals simulates some of the charge compression that would otherwise have been left out of the free-atom calculations.

<sup>17</sup>The kinetic energy throughout the discussion refers to the expectation of  $-\frac{1}{2}\nabla^2$  (in atomic units). Thus the total kinetic energy is the sum of orbital kinetic energies. Within local-density theory there is a contribution to the total kinetic energy from the correlation energy. For the present discussion this term will be counted as part of the potential energy, a relabeling that does not affect the result but simplifies the notation.

<sup>18</sup>J. C. Slater, *Quantum Theory of Molecules and Solids* (McGraw-Hill, New York, 1974), Vol. IV, p. 35; C. O. Almladh and U. von Barth, *Phys. Rev. B* **13**, 3307 (1976).

<sup>19</sup>A similar analysis of the total-energy error based on eigenvalue errors is found in Ref. 2.

<sup>20</sup>The calculations assumed a common Wigner-Seitz radius, 2.9 bohr, for both structures. This is a slightly smaller radius than that corresponding to the theoretical minimum bcc energy (Ref. 5).

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<sup>22</sup>The pressure error will depend on the extent to which the core is sensitive to changes in density, and the extent to which the pressure is affected by the resulting violation of the virial theorem. In the Mo structure-change calculation the difference between the fully self-consistent fcc pressure and the frozen-core pressure was less than 2%.