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Generalized local-density approximation for spherical potentials

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An alternative density functional for the spherical approximation of cell potentials is formulated. It relies on overlapping atomic spheres for the calculation of the kinetic energy, similar to the atomic sphere approximation (ASA), however, a shape correction is used that has the same form as the interstitial treatment in the nonoverlapping muffin-tin (MT) approach. The intersite Coulomb energy is evaluated using the Madelung energy as computed in the MT approach, while the on-site Coulomb energy is calculated using the ASA. The Kohn-Sham equations for the functional are then solved self-consistently. The ASA is known to give poor elastic constants and good point defect energies. Conversely the MT approach gives good elastic constants and poor point defect energies. The proposed new functional maintains the simplicity of the spherical potentials found in the ASA and MT approaches, but gives good values for both elastic constants and point defects. This solution avoids a problem, absent in the ASA but suffered by the MT approximation, of incorrect distribution of site charges when charge transfer is large. Relaxation of atomic positions is thus facilitated. Calculations confirm that the approach gives similar elastic constants to the MT approximation, and defect formation energies similar to those obtained with ASA. [S0163-1829(99)09631-9]

I. INTRODUCTION

Traditional band structure techniques based on the multiple scattering Green function approach[1] require the spherical approximation of the electronic cell potentials. Although great progress has been made in the development of full-potential multiple scattering theory,[2] calculations using spherical potentials still remain the norm because of their speed and simplicity. There are two ways that the spherical approximation is invoked. The first is the so-called ''muffin-tin'' (MT) approximation,[3] where space is divided into nonoverlapping spherical volumes centered at each nucleus within which the potential is spherical, and the interstitial region between these spheres, where the potential is constant. The second form is the ''atomic sphere approximation'' (ASA),[4] which approximates the space by a collection of spheres, centered at the nuclei, whose volume equals the volume of the corresponding atomic cell.

Both of these approximations have been quite successful in predicting a wide range of properties of metals and alloys. However, they suffer severe limitations. In particular, the ASA cannot give reliable energy differences between structures that differ in the shape of the atomic cell, thus it is unable to reliably predict the stable structure for materials. This is mainly due to the incorrect Coulomb energy contribution from the interstitial charge in the ASA. The interstitial charge plays an important role in determining structural properties, but the ASA is the poorest in describing this charge. On the other hand, the MT approximation does a reasonably good job of describing the interstitial charge for transition metals, as reflected in the good elastic constants obtained for several materials using the MT approximation.[5] However, the MT approach usually fails in systems where there is a large charge transfer. It cannot in general even predict the correct amount of charge transfer in these systems. This is because, in the reconstruction of the effective potential, the interstitial charge is averaged and then redistributed over all the atomic cells. A local change in the interstitial charge around a defect is transferred by the averaging process to the far reaches of the unit cell. This introduces an artificial charge transfer when the real electron density in the interstitial regions of different atomic cells is different. This problem becomes worse for large unit cells, such as those often used in connection with the locally self-consistent multiple scattering (LSMS) technique.[6] In these applications, even a small error in the interstitial charge due to the MT approximation can give an artificial charge transfer between very distant atoms in the unit cell. This can lead to a large error in the Coulomb energy because of the large size of the unit cell.

There has been work directed at overcoming these difficulties. One approach is to add a perturbative correction to the ASA density functional by replacing the Coulomb energy by a more accurate term using the MT charge density.[7] This has been improved to include corrections due to the full-cell charge density to the ASA total energy.[8] This approach allows one to calculate elastic constants accurately for transition metals. However the correction term is not self-consistent, thus its reliability cannot be affirmed. Alternatively one may employ a full potential approach. However, experience in the past decade has shown that a general, fully self-consistent full-potential approach for MST would be rather cumbersome.

In consideration of the fact that for some time to come a majority of MST calculations will use a spherical approximation, we propose a scheme that combines the strengths of each approach, overcomes their limitations, and maintains the simplicity of spherical approaches. We will present a new energy functional, from which a self-consistent procedure is derived. This procedure contains a bandstructure part that is based on MST within the ASA plus a shape correction, and an intersite Coulomb energy part that is analogous to the standard MT approach. We demonstrate this new approach with calculations of elastic constants of a few transition metals, and the vacancy formation energy of copper.

II. THE ELECTRON DENSITY FUNCTIONAL

The total energy functional in a typical local density functional approach[9,10] is written as

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

where the three terms on the right are the kinetic energy, Coulomb energy, and exchange-correlation energy, respectively for the electron density $\rho(\mathbf{r})$. The kinetic energy is given by

$$T=\sum_{\epsilon<E_F}\epsilon-\int d^3\mathbf{r}\,\rho(\mathbf{r})V_{\mathrm{eff}}(r), \tag{2}$$

where $\Sigma\epsilon$ is the band energy sum obtained using one of the standard bandstructure approaches to the Shrödinger equation for the potential V_{eff}, and E_F is the Fermi energy for the electrons.

The total Coulomb energy, in atomic units, is,

$$U[\rho]=\int d^3\mathbf{r}\int d^3\mathbf{r}'\frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}+\sum_{ij,i\neq j}\frac{Z_iZ_j}{|\mathbf{R}_i-\mathbf{R}_j|}-2\sum_i\int d^3\mathbf{r}\frac{Z_i\rho(\mathbf{r})}{|\mathbf{R}_i-\mathbf{r}|}, \tag{3}$$

where Z_i are the atomic numbers and $\mathbf{R}_i$ are the positions of the nuclei. We separate U into site diagonal and site off-diagonal parts,

$$U[\rho]=U^{(\mathrm{o})}+\sum_i U_i^{(\mathrm{d})}[\rho_i,Z_i], \tag{4}$$

with

$$U_i^{(\mathrm{d})}[\rho_i,Z_i]=\int d^3\mathbf{r}\int d^3\mathbf{r}'\frac{\rho_i(\mathbf{r})\rho_i(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}-2\int d^3\mathbf{r}\frac{Z_i\rho_i(\mathbf{r})}{|\mathbf{r}|}. \tag{5}$$

The Kohn-Sham effective potential[10] V_{eff} is obtained from the requirement that the total energy functional is variational with respect to the charge density,

$$\frac{\delta E[\rho]}{\delta\rho(\mathbf{r})}=-V_{\mathrm{eff}}(r)+\frac{\delta W[\rho]}{\delta\rho(\mathbf{r})}=0, \tag{6}$$

where

$$W[\rho]=U[\rho]+E_{\mathrm{xc}}[\rho]. \tag{7}$$

In order to find a generalized approach to calculate the Coulomb energy which reduces to the standard Coulomb energy involving the Madelung term in the limit of MT approximation, we introduce a reference system composed of point charges $Q_i^{\text{ASA-MT}}$ at the lattice sites and a compensating uniform electron density,

$$\rho^{\mathrm{comp}}=\frac{\sum_i Q_i^{\text{ASA-MT}}}{\sum_i \Omega_i}. \tag{8}$$

We will see later that it is the different definitions for the charge $Q_i^{\text{ASA-MT}}$ that gives rise to the different energy expressions in the ASA, MT, and ASA-MT approximations. The electrostatic energy of the reference system is given by a Madelung sum and can also be separated into site diagonal and off-diagonal parts,

$$\begin{aligned}U_{\mathrm{Mad}}[\rho]&=U_{\mathrm{Mad}}^{(\mathrm{o})}+\sum_i U_i^{(\mathrm{d})}[\rho^{\mathrm{comp}},Q_i^{\text{ASA-MT}}]\\&=\frac{1}{2}\sum_{ij}Q_i^{\text{ASA-MT}}M_{ij}Q_j^{\text{ASA-MT}},\end{aligned} \tag{9}$$

where M_{ij} is the Madelung matrix. Upon adding and subtracting the Madelung energy of the reference system,

$$W[\rho]=\sum_i W_i[\rho]+U^{(\mathrm{o})}[\rho]+\frac{1}{2}\sum_{ij}Q_i^{\text{ASA-MT}}M_{ij}Q_j^{\text{ASA-MT}}-U_{\mathrm{Mad}}^{(\mathrm{o})}[\{Q_i^{\text{ASA-MT}}\}], \tag{10}$$

and

$$W_i[\rho]=U_i^{(\mathrm{d})}[\rho_i,Z_i]-U_i^{(\mathrm{d})}[\rho^{\mathrm{comp}},Q_i^{\text{ASA-MT}}]+E_{\mathrm{xc}}[\rho_i], \tag{11}$$

where $\rho_i=\rho(\mathbf{r})\sigma_i(\mathbf{r})$ and $\sigma_i(\mathbf{r})$ is the cell shape function for cell i. We now look for an approximation such that $U^{(\mathrm{o})}[\rho]=U_{\mathrm{Mad}}^{(\mathrm{o})}[\{Q_i^{\text{ASA-MT}}\}]$.

The spherical shape approximations such as MT or ASA can be thought of as approximations to the explicit form of the Coulomb and exchange-correlation energy $W[\rho]$ as a functional of the electron density $\rho(\mathbf{r})$. Approximate forms for $W[\rho]$ can be constructed by introducing auxiliary densities that in turn depend on $\rho(\mathbf{r})$. A general form for such a density that covers both the MT and ASA cases consists of a spherical part, $\rho_i^{\mathrm{S}}(r)$, that is defined over a sphere of radius $r_{i\mathrm{S}}$, an interstitial part, ρ^{int}, and an additional term containing ΔQ_i, a charge that will be defined later. The spherical part inside the MT sphere is easily defined as the angular average of the full charge density,

$$\rho_i^{\mathrm{S}}(r)=\frac{1}{4\pi}\int_i d\Omega\,\rho_i(\mathbf{r}),\quad r<r_{i\mathrm{MT}}. \tag{12}$$

If $r_{i\mathrm{S}}>r_{i\mathrm{MT}}$, then for r outside the MT radius but inside $r_{i\mathrm{S}}$, the definition of $\rho^{\mathrm{S}}(r)$ in terms of the full charge density is not clear. Specifically, the site electron density is zero in those volumes that are inside r_{S} but outside the WS cell. In this case the standard interpretation is that a space of equal volume outside r_{S} but inside the WS cell is mapped into this volume, and then an angular average of the charge is performed. Thus

$$\rho_i^{\mathrm{S}}(r)=\frac{1}{4\pi}\int_i d\Omega\,\rho_i(\mathbf{r}'[\mathbf{r}]),\quad r_{i\mathrm{S}}>r>r_{i\mathrm{MT}}, \tag{13}$$

where $\mathbf{r}'[\mathbf{r}]$ indicates the mapping. This mapping leaves an interstitial space of volume $\Omega_i - \Omega_i^{\mathrm{S}}$, that lies inside the ''ith'' WS cell. Where Ω_i is the cell volume, and

$$\Omega_i^{\mathrm{S}} = \frac{4\pi}{3} r_{i\mathrm{S}}^3 .$$

This volume vanishes when $r_{i\mathrm{S}} = r_{i\mathrm{WS}}$. We introduce the function $s_i(\mathbf{r}) = 1\ (0)$ for points, $\mathbf{r}$, inside (outside) this interstitial region. If the electron density is nearly flat in the outer portion of the cell or if $r_{i\mathrm{S}}$ is very close to $r_{i\mathrm{MT}}$ the exact nature of the mapping in Eq. (13) is inconsequential. We adhere to the ASA convention and will therefore leave the mapping unspecified with the understanding that it will typically have little impact on results. The interstitial charge density is determined by the charge in the entire interstitial volume, i.e., that outside the MT spheres,

$$\rho^{\mathrm{int}} = \frac{1}{\Omega^{\mathrm{int}}} \sum_i \left[Z_i - \int d^3\mathbf{r}\, \rho_i^{\mathrm{S}}(r) \Theta(r_{i\mathrm{MT}} - r) \right], \tag{14}$$

where $\Omega^{\mathrm{int}} = \Sigma_i (\Omega_i - 4\pi/3 r_{i\mathrm{MT}}^3)$. Note that this definition is independent of $r_{i\mathrm{S}}$, and in the limit of $r_{i\mathrm{S}} = r_{i\mathrm{WS}}$, ρ^{int} remains unchanged although the volume it occupies goes to zero. Finally, we add a number of electrons ΔQ_i to adjust the total site charge. As we will see later, this term is required if one includes a shape correction to the ASA. If $\Delta Q_i = 0$ the standard MT(ASA) densities are recovered when $r_{i\mathrm{S}} = r_{i\mathrm{MT}}(r_{i\mathrm{WS}})$. Combining all three terms, we have

$$\rho_i^{\mathrm{ASA\text{-}MT}}(\mathbf{r}) = \rho_i^{\mathrm{S}}(r) + \Delta Q_i \delta(r - r_{i\mathrm{S}}) + \rho^{\mathrm{int}} s_i(\mathbf{r}). \tag{15}$$

The region occupied by ρ^{int} has zero volume when $r_{\mathrm{S}} = r_{\mathrm{WS}}$. When $r_{\mathrm{S}} = r_{\mathrm{MT}}$, s_i is the volume in the cell that is outside the ''muffin-tin.'' At values of $r_{i\mathrm{S}}$ between $r_{i\mathrm{MT}}$ and $r_{i\mathrm{WS}}$, the shape of this electron density becomes complicated because $s_i(\mathbf{r})$ is complicated. It is still, however, usable and leads to spherical potentials, because it only enters the energy as a prefactor to ρ^{int} which depends only on the spherical part of the electron density. Furthermore, this form provides a continuous link between the MT and ASA approaches. The calculations presented in this work are done with $r_{i\mathrm{S}} = r_{i\mathrm{WS}}$.

We follow the standard MT and ASA procedure of approximating W_i by replacing ρ_i in E_{xc} and $U_i^{(\mathrm{d})}$ by $\rho_i^{\mathrm{ASA\text{-}MT}}$, and replacing ρ^{comp} by

$$\rho_{\mathrm{comp}}^{\mathrm{ASA\text{-}MT}} = \rho^{\mathrm{comp}} [\Theta(r_{i\mathrm{S}} - r) + s_i(r)], \tag{16}$$

so that

$$\begin{aligned} W_i^{\mathrm{ASA\text{-}MT}}[\rho] &= U_i^{(\mathrm{d})}[\rho_i^{\mathrm{ASA\text{-}MT}}, Z_i] - U_i^{(\mathrm{d})}[\rho_{\mathrm{comp}}^{\mathrm{ASA\text{-}MT}}, Q_i^{\mathrm{ASA\text{-}MT}}] + E_{\mathrm{xc}}[\rho_i^{\mathrm{S}}] + \rho^{\mathrm{int}} \epsilon_{\mathrm{xc}}(\rho^{\mathrm{int}})(\Omega_i - \Omega_i^{\mathrm{S}}) + \mu_{\mathrm{xc}}(\rho_i^{\mathrm{S}}(r_{i\mathrm{S}}))\Delta Q_i \\ &= \int d^3\mathbf{r}\, d^3\mathbf{r}' \frac{\rho_i^{\mathrm{ASA\text{-}MT}}(\mathbf{r}) \rho_i^{\mathrm{ASA\text{-}MT}}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} - 2 \int d^3\mathbf{r} \frac{\rho_i^{\mathrm{ASA\text{-}MT}}(\mathbf{r}) Z_i}{r} - \int d^3\mathbf{r}\, d^3\mathbf{r}' \frac{\rho_{\mathrm{comp}}^{\mathrm{ASA\text{-}MT}}(\mathbf{r}) \rho_{\mathrm{comp}}^{\mathrm{ASA\text{-}MT}}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \\ &\quad + 2 \int d^3\mathbf{r} \frac{\rho_{\mathrm{comp}}^{\mathrm{ASA\text{-}MT}}(\mathbf{r}) Q_i^{\mathrm{ASA\text{-}MT}}}{r} + E_{\mathrm{xc}}[\rho_i^{\mathrm{S}}] + \rho^{\mathrm{int}} \epsilon_{\mathrm{xc}}(\rho^{\mathrm{int}})(\Omega_i - \Omega_i^{\mathrm{S}}) + \mu_{\mathrm{xc}}(\rho_i^{\mathrm{S}}(r_{i\mathrm{S}}))\Delta Q_i , \end{aligned} \tag{17}$$

where μ_{xc} and ϵ_{xc} are the exchange-correlation potential and energy density, respectively. We have used a linear expansion to obtain the exchange-correlation energy which is valid for the case where ρ_i^{S} for $r > r_{\mathrm{MT}}$ is slowly varying and large compared to the electron density associated with ΔQ_i. We continue following the standard MT and ASA procedure and take $U^{(\mathrm{o})}$ to be equal to $U_{\mathrm{Mad}}^{(\mathrm{o})}$. They therefore cancel in Eq. (10) leaving the Madelung energy,[11] explicitly,

$$W^{\mathrm{ASA\text{-}MT}}[\rho] = \sum_i W_i^{\mathrm{ASA\text{-}MT}}[\rho] + \frac{1}{2} \sum_{ij} Q_i^{\mathrm{ASA\text{-}MT}} M_{ij} Q_j^{\mathrm{ASA\text{-}MT}}. \tag{18}$$

At this point we have a fairly general form for the density functional that depends on the electron density only through $\rho_i^{\mathrm{ASA\text{-}MT}}$ and $Q_i^{\mathrm{ASA\text{-}MT}}$. The density $\rho_i^{\mathrm{ASA\text{-}MT}}$ depends on the spherical average of $\rho(\mathbf{r})$ and on ΔQ_i which has not, at this point, been specified. Likewise the dependence of $Q_i^{\mathrm{ASA\text{-}MT}}$ on $\rho(\mathbf{r})$ has yet to be specified. It is convenient to define the cell charge,

$$Q_i^{\mathrm{cell}} = \int d^3\mathbf{r}\, \rho_i^{\mathrm{ASA\text{-}MT}} = Q_i^{\mathrm{S}} + \Delta Q_i + \rho^{\mathrm{int}}(\Omega_i - \Omega_i^{\mathrm{S}}), \tag{19}$$

where

$$Q_i^{\mathrm{S}} = \int_0^{r_{i\mathrm{S}}} d^3\mathbf{r}\, \rho_i^{\mathrm{S}}(\mathbf{r}). \tag{20}$$

The sum over all sites of the cell charge gives the total number of electron is the system and is used to determine the Fermi level. The essence of the various spherical approximations, ASA or MT, is the choice of $r_{i\mathrm{S}}$ and $Q_i^{\mathrm{ASA\text{-}MT}}$. The ASA, where $\Delta Q_i = 0$ and $r_{i\mathrm{S}} = r_{i\mathrm{WS}}$, is derived by taking

$$\lim_{\mathrm{ASA}} Q_i^{\mathrm{ASA\text{-}MT}} = Q_i^{\mathrm{ASA}} = Z_i - Q_i^{\mathrm{cell}}. \tag{21}$$

It is easy to see that, in the ASA, $\rho^{\mathrm{comp}} = 0$. One arrives at the MT approximation, where $\Delta Q_i = 0$ and $r_{i\mathrm{S}} = r_{i\mathrm{MT}}$, by setting

$$\lim_{\mathrm{MT}} Q_i^{\mathrm{ASA\text{-}MT}} = Q_i^{\mathrm{MT}} = Z_i - Q_i^{\mathrm{cell}} + \rho^{\mathrm{int}} \Omega_i . \tag{22}$$

TABLE I. Calculated equilibrium lattice constants a and bulk moduli B_0 for Cu, Ni, and Fe as compared with experimental data.

	a (atomic units)		B_0 (Mbar)	
	Expt.	ASA-MT	Expt.	ASA-MT
Cu	6.83	6.78	1.37	1.43
Ni	6.66	6.59	1.80	1.82
Fe	5.42	5.28	1.78	0.98

This leads to $\rho^{\text{comp}}=\rho^{\text{int}}$. In order to benefit from the more accurate description of the Madelung Coulomb energy in the MT approximation we follow the MT procedure and make the following definition:

$$Q_i^{\text{ASA-MT}}=Z_i-Q_i^{\text{cell}}+\rho^{\text{int}}\Omega_i. \tag{23}$$

This gives a Madelung energy that corresponds to $\rho^{\text{comp}}=\rho^{\text{int}}$ which is the same interstitial charge as in the MT case. However, the major difference between the MT approach and the ASA-MT approach is that the interstitial part of the on-site Coulomb energy is calculated using ρ^{int} in the MT approach, but using ρ_i^{S} in the ASA-MT approach.

We now turn our attention to the definition of ΔQ_i. This quantity is introduced as a means of assigning a physically reasonable amount of charge to the cell density $\rho^{\text{ASA-MT}}$. If $r_{\text{S}}=r_{\text{MT}}$ and all atoms are equivalent then ΔQ_i is zero because the total number of electrons in the cell must equal Z_i. However, if there are inequivalent atoms, ΔQ_i is given by the integrated difference over the interstitial volume of cell i between the electron density and ρ^{int}. In the MT approximation the electron densities in the interstitial regions are given by the plane wave solutions for a constant potential, V_{MT} that match to the MST solutions on the surfaces of the MT spheres. We extend this definition to larger values of r_{S} by defining,

$$\Delta Q_i=q_i-\rho^{\text{int}}(\Omega_i-\Omega_i^{\text{S}}), \tag{24}$$

where q_i is the integral, of the square of plane waves matched to the MST solutions at r_{S}, from the sphere of radius r_{S} to the WS cell boundary with the convention that contributions to the integral inside r_{S} are negative and those from outside r_{S} are positive. As r_{S} increases the magnitude of q_i is reduced because the volume of integration inside r_{S} approaches the volume outside. When $r_{\text{S}}=r_{\text{MT}}$, for a given self-consistent iteration, the Fermi energy is independent of whether or not ΔQ_i is set to zero because the sum of all ΔQ_i is zero by construction. However, for other choices of r_{S} the Fermi level and hence the eigenvalue sum will be affected at each iteration. Replacing ΔQ_i in Eqs. (23) and (19) by its definition according to Eq. (24) we obtain

$$Q_i^{\text{ASA-MT}}=Z_i-Q_i^{\text{S}}-q_i+\rho^{\text{int}}\Omega_i \tag{25}$$

and

$$Q_i^{\text{cell}}=Q_i^{\text{S}}+q_i. \tag{26}$$

Using the definitions of $\rho_i^{\text{ASA-MT}}$, ρ^{comp}, and $Q_i^{\text{ASA-MT}}$ in Eq. (17) we find,

$$W_i^{\text{ASA-MT}}[\rho_i]=\int d^3\mathbf{r}\,d^3\mathbf{r}'\frac{\rho_i^{\text{S}}(r)\rho_i^{\text{S}}(r')}{|\mathbf{r}-\mathbf{r}'|}-2\int d^3\mathbf{r}\frac{\rho_i^{\text{S}}(r)Z_i}{r}-\frac{6[\rho^{\text{int}}\Omega_i^{\text{S}}]^2}{5r_{i\text{S}}}+4\pi\rho^{\text{int}}Q_i^{\text{ASA-MT}}r_{i\text{S}}^2+E_{\text{xc}}[\rho_i^{\text{S}}]$$
$$+\rho^{\text{int}}\epsilon_{\text{xc}}(\rho^{\text{int}})(\Omega_i-\Omega_i^{\text{S}})+\mu_{\text{xc}}(\rho_i^{\text{S}}(r_{i\text{S}}))\Delta Q_i+\Delta Q_i\left(\frac{\Delta Q_i+2(Q_i^{\text{S}}-Z_i)}{r_{i\text{S}}}\right). \tag{27}$$

The requirement that the functional derivative of the energy with respect to the electron density be zero gives the one-electron effective potential. There are two contributions to the V_{eff}. The first is from the derivative with respect to the explicit spherical electron density, $\rho_i^{\text{S}}(r)$, which gives a contribution to the potential for all r inside $r_{i\text{S}}$. The second contribution comes from the derivative with respect to ρ^{int} which depends implicitly on $\rho_i^{\text{S}}(r)$ for $r<r_{\text{MT}}$ and therefore contributes only to the potential inside the MT radius. This introduces a discontinuity in the effective potential at r_{MT}, which must be dealt with explicitly in the solution of radial wave equations. Using Eqs. (25) and (14), we can take the

TABLE II. Shear moduli for Cu, Ni, and Fe calculated at the experimental lattice constants. All numbers are in Mbar.

	$C_{11}-C_{12}$				C_{44}			
	Exp	MT	ASA	ASA-MT	Exp	MT	ASA	ASA-MT
Cu	0.47	0.36	−0.48	0.36	0.75	1.60	−0.96	1.56
Ni	0.99	0.85	0.03	0.83	1.25	2.21	−0.65	2.11
Fe	0.96	1.08	0.63	1.04	1.12	1.63	−0.93	1.54

derivative with respect to $\rho(r)$ of the Coulomb parts of the potential energy and obtain the electrostatic part of the potential,

$$\phi_i^{\text{ASA-MT}}=\frac{\delta U^{\text{ASA-MT}}}{\delta\rho_i(r)}=\int d^3\mathbf{r}'\frac{2\rho_i^{\text{S}}(r)}{|\mathbf{r}-\mathbf{r}'|}-\frac{2Z_i}{r}-V_i^0 -V_1\Theta(r_{i\text{MT}}-r),\quad r<r_{i\text{S}}, \tag{28}$$

where V_i^0 and V_1 are constants,

$$V_i^0=\sum_j M_{ij}Q_j^{\text{ASA-MT}}+4\pi\rho^{\text{int}}r_{i\text{S}}^2-\frac{2\Delta Q_i}{r_{i\text{S}}}, \tag{29}$$

and

$$V_1=\sum_i V_{i1}$$

$$\Omega^{\text{int}}V_{i1}=\sum_j \Omega_i M_{ij}Q_j^{\text{ASA-MT}}+\frac{4\pi}{5}\rho^{\text{int}}\Omega_i^{\text{S}}r_{i\text{S}}^2+4\pi r_{i\text{S}}^2Q_i^{\text{ASA-MT}} +(\Omega_i-\Omega_i^{\text{S}})\left[\frac{4\pi}{3}\rho^{\text{int}}r_{i\text{S}}^2+\frac{2Q_i^{\text{ASA-MT}}}{r_{i\text{S}}}\right]. \tag{30}$$

V_i^0 is the potential at the origin from a lattice of point charges in a compensating uniform background but with the contribution from the uniform charge within $r_{i\text{S}}$ subtracted and the potential from ΔQ_i added. V_1 is from derivatives with respect to ρ^{int} and is a shift in the potential at the MT radius, similar to the MT step in the case of the MT approximation.

The derivative with respect to q_i involves the density in the interstitial region and is site dependent. It can potentially give contributions to the potential that are not spherical and are site dependent. Recall however, that the charge q_i is derived from a sum of free electron solutions in a constant potential, $\overline{V}_i$. The appropriate value of this constant is determined by minimizing the energy with respect to q_i. Noting that $\delta U^{\text{ASA-MT}}/\delta q_i=\int d^3\mathbf{r}\,\delta U^{\text{ASA-MT}}/\delta\rho_i^{\text{S}}(r)\,\delta(r-r_{i\text{S}})$, we obtain

$$\overline{V}_i=\phi_i^{\text{ASA-MT}}(r_{i\text{S}})+\mu_{\text{xc}}[\rho_i^{\text{S}}(r_{i\text{S}})]. \tag{31}$$

This implies that the MST solution is to be referenced from a different constant potential for each site. This is inconsistent with determination of the eigenvalue sum within the MST approach. However, we are at liberty to solve the MST equations with a site independent constant potential, $\overline{V}$, and afterwards correct the eigenvalue sum to any desired level of perturbation in the difference between $\overline{V}$ and $\overline{V}_i$. We chose to include only first order perturbation corrections, and further choose the value of $\overline{V}$ that renders these to be zero, namely,

$$\overline{V}=\frac{\sum_i q_i\overline{V}_i}{\sum_i q_i}. \tag{32}$$

Finally, collecting the pieces discussed above and setting the zero of energy for the potential to $\overline{V}$ we have the ASA-MT energy functional,

$$E[\rho]=T^{\text{ASA-MT}}[\rho]+U^{\text{ASA-MT}}[\rho]+E_{\text{xc}}^{\text{ASA-MT}}[\rho], \tag{33}$$

where

$$T^{\text{ASA-MT}}[\rho]=\sum_{\epsilon<E_F}\epsilon-\sum_i\int d^3\mathbf{r}\,\rho_i^{\text{S}}(r)V_{i\text{eff}}(r), \tag{34}$$

$$U^{\text{ASA-MT}}[\rho]=\sum_i\left\{-\int_0^{r_{i\text{S}}}d^3\mathbf{r}\frac{\rho_i^{\text{S}}(r)2Z_i}{r}+2\int d^3\mathbf{r}\,\rho_i^{\text{S}}(r)\int^r d^3\mathbf{r}'\frac{\rho_i^{\text{S}}(r')}{r'}\right\}+\sum_i\left\{-\frac{6}{5}\sum_i\frac{[\rho^{\text{comp}}\Omega_i^{\text{S}}]^2}{r_{i\text{S}}} +4\pi\rho^{\text{comp}}\sum_i Q_i^{\text{ASA-MT}}r_{i\text{S}}^2+\Delta Q_i\left(\frac{\Delta Q_i+2(Q_i^{\text{S}}-Z_i)}{r_{i\text{S}}}\right)\right\}+\frac{1}{2}\sum_{ij}Q_i^{\text{ASA-MT}}M_{ij}Q_j^{\text{ASA-MT}}, \tag{35}$$

and

$$E_{\text{xc}}^{\text{ASA-MT}}=\sum_i\{E_{\text{xc}}[\rho_i^{\text{S}}]+\rho^{\text{int}}\epsilon_{\text{xc}}(\rho^{\text{int}})(\Omega_i-\Omega_i^{\text{S}})+\mu_{\text{xc}}[\rho_i^{\text{S}}(r_{\text{S}})]\Delta Q_i\}. \tag{36}$$

The exchange-correlation potential, $\mu_{\text{xc}}^{\text{ASA-MT}}[\rho_i]=\delta E_{\text{xc}}^{\text{ASA-MT}}/\delta\rho_i$, is given by

$$\mu_{\text{xc}}^{\text{ASA-MT}}[\rho_i]=\mu_{\text{xc}}[\rho_i^{\text{S}}(r)]-\mu_{\text{xc}}[\rho^{\text{int}}]\Theta(r_{i\text{MT}}-r)\frac{\Omega_i-\Omega_i^{\text{S}}}{\Omega^{\text{int}}}+\mu_{\text{xc}}'[\rho_i^{\text{S}}(r)]\frac{\delta(r-r_{i\text{S}})}{4\pi r_{i\text{S}}^2}\Delta Q_i. \tag{37}$$

The self-consistent effective potential is then,

$$V_{i\mathrm{eff}}(r)=\frac{-2Z_i}{r}+\frac{2}{r}\int_0^r d^3\mathbf{r}'\,\rho^{\mathrm{S}}(r')+2\int_r^{r_{i\mathrm{S}}} d^3\mathbf{r}'\frac{\rho^{\mathrm{S}}(r')}{r'}-V_i^0-\left[V_1+\mu_{\mathrm{xc}}(\rho^{\mathrm{int}})\frac{(\Omega_i-\Omega_i^{\mathrm{S}})}{\Omega^{\mathrm{int}}}\right]\Theta(r_{i\mathrm{MT}}-r)+\mu_{\mathrm{xc}}[\rho_i^{\mathrm{S}}(r)]-\overline{V}$$
$$+\mu'_{\mathrm{xc}}[\rho_i^{\mathrm{S}}(r)]\frac{\delta(r-r_{i\mathrm{S}})}{4\pi r_{i\mathrm{S}}^2}\Delta Q_i, \qquad (38)$$

where $\mu'_{\mathrm{xc}}(x)$ is the derivative of $\mu_{\mathrm{xc}}(x)$ with respect to x. This completes our derivation of the new energy functional. The last term in the effective potential involving a delta function at $r=r_{i\mathrm{S}}$ is neglected in our calculations. This term introduces a small change in the phase shifts of the corresponding spherical potentials.

In the calculations described below in which we used $r_{\mathrm{S}}=r_{\mathrm{WS}}$, we have $\Delta Q_i=q_i$, and the energy becomes

$$E[\rho]=\sum_{\epsilon<E_F}\epsilon-\sum_i\int d^3\mathbf{r}\,\rho_i^{\mathrm{S}}(r)V_{i\mathrm{eff}}(r)+\sum_i\left\{-\int_0^{r_{i\mathrm{WS}}}d^3\mathbf{r}\frac{\rho_i^{\mathrm{S}}(r)2Z_i}{r}-\frac{2Z_iq_i}{r_{i\mathrm{WS}}}+2\int d^3\mathbf{r}\,\rho_i^{\mathrm{S}}(r)\int^r d^3\mathbf{r}'\frac{\rho_i^{\mathrm{S}}(r')}{r'}\right\}$$
$$+\sum_i\left\{\frac{2q_iQ_i^{\mathrm{S}}+q_i^2}{r_{i\mathrm{WS}}}-\frac{6}{5}\frac{[\rho^{\mathrm{comp}}\Omega_i]^2}{r_{i\mathrm{WS}}}+4\pi\rho^{\mathrm{comp}}Q_i^{\mathrm{ASA\text{-}MT}}r_{i\mathrm{WS}}^2\right\}+\sum_i\{E_{\mathrm{xc}}[\rho_i^{\mathrm{S}}]+\mu_{\mathrm{xc}}(\rho_i^{\mathrm{S}}(r_{\mathrm{WS}}))q_i\}$$
$$+\frac{1}{2}\sum_{ij}Q_i^{\mathrm{ASA\text{-}MT}}M_{ij}Q_j^{\mathrm{ASA\text{-}MT}}, \qquad (39)$$

where

$$V_{i\mathrm{eff}}(r)=\frac{2}{r}\int_0^r d^3\mathbf{r}'\,\rho^{\mathrm{S}}(r')+2\int_r^{r_{i\mathrm{WS}}}d^3\mathbf{r}'\frac{\rho^{\mathrm{S}}(r')}{r'}-\frac{2Z_i}{r}-V_i^0-V_1\Theta(r_{i\mathrm{MT}}-r)+\mu_{\mathrm{xc}}[\rho_i^{\mathrm{S}}(r)]-\overline{V} \qquad (40)$$

and

$$Q_i^{\mathrm{ASA\text{-}MT}}=Q_i^{\mathrm{S}}+q_i+\rho^{\mathrm{int}}\Omega_i-Z_i. \qquad (41)$$

We note that the ASA-MT approach actually represents a spectrum of approximations, according to the choice of r_{S}, since there is no restriction within the approach on the value of r_{S}. At one end of the spectrum, when $r_{\mathrm{S}}=r_{\mathrm{WS}}$, we can set $\Delta Q_i=0$ and have essentially a conventional ASA. In this case, the above derivation provides a variational energy functional for the ASA. It is interesting to note that from this derivation the zero scale of the energy in the ASA is not arbitrary, but is determined by Eq. (32), which in the ASA limit is simply the weighted average of the ASA potential at r_{WS} over all atoms. Only with this choice of the energy zero the variational property of the total energy is maintained.

III. APPLICATIONS

To test our theory, we calculated the second order elastic constants of Cu, Ni, and Fe. Although the ASA usually gives reasonable bulk moduli, it is known to give negative shear modulus for many systems. On the other hand, MT approximation typically gives fair elastic constants for transition metals.[5] We used the LSMS to calculate the equilibrium lattice constants, bulk modulus (at the experimental lattice constants), B_0, and the shear moduli at experimental lattice constants $C_{11}-C_{12}$, and C_{44}, for Cu, Ni, and Fe. The results are compared with the experimental values in Tables I, II, and III. As in a typical LDA calculation, the error in the bulk modulus varies from 10% to 50%. We have tabulated only the ASA-MT values of the bulk moduli because the ASA-MT agrees almost exactly with both the MT and ASA. The bulk modulus from ASA-MT for Fe appears to be surprisingly small. This is because at the experimental lattice constant the LDA gives a moment that is too large ($2.34\mu_B$ for the ASA-MT). At the ASA-MT equilibrium lattice constant, of 5.28 atomic units, the moment is $2.14\mu_B$ and the bulk modulus is 2.04 MBar. The lattice constant, moment, and bulk modulus agree very well with the MT results of Moruzzi *et al.*[12] The error in $C_{11}-C_{12}$ is reasonably small, while the calculated values for C_{44} are consistently off by almost a factor of two. The ASA-MT approach gives essentially the same values as the MT for $C_{11}-C_{12}$ and C_{44} for all materials, but the ASA gives mostly negative values, as expected. We speculate that the error in the ASA-MT values of C_{44} is due mostly to the nonspherical charge distribution, since a full potential method such as FLAPW usually gives much more accurate values for C_{44}.

Another test of the method is to calculate the vacancy formation energy. This is usually calculated using the ASA since the MT approximation does not treat the charge transfer associated with vacancies very well. We calculated the vacancy formation energy of Cu for an unrelaxed lattice,

TABLE III. Vacancy formation energy for Cu compared to the experimental value, and the calculated charge on the vacancy site. Note the calculated values are for unrelaxed lattices. The charge transfer in parentheses for the MT case is before the interstitial average is taken.

	Exp	MT	ASA	ASA-MT
Vacancy energy	1.3 eV	4.3 eV	2.8 eV	2.4 eV
Vacancy charge	—	−1.133 (−0.876)	−0.848	−0.857

using the MT approximation, the ASA, and the ASA-MT approach. The results are listed in Table III and are compared with the experimental value.[13] In this table we also compare the amount of charge on the vacancy site given by three methods. It is evident that the ASA and the ASA-MT results are very close in this case, and both are significantly better than the MT value. The remaining difference between the ASA-MT value and the experimental value is probably from nonspherical charge effects (especially the dipole terms) and energy due to lattice relaxation. The comparison of the vacancy charge highlights the fact that the ASA-MT approach yields a charge density that is significantly closer to the ASA charge density than the MT one.

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