

Self-Consistent Energy Bands and Cohesive Energy of γ -Fe Using Two Forms of the Warped-Muffin-Tin Potential*

Leonard Kleinman and Robert Shurtliff

Department of Physics, University of Texas, Austin, Texas 78712

(Received 30 June 1971)

We recently reported that, using a self-consistent warped-muffin-tin potential which was a straightforward generalization of the ordinary muffin-tin potential, we were unable to obtain a negative cohesive energy for γ -Fe. We here report that by using another self-consistent warped-muffin-tin potential which is more akin to the true crystal potential, we obtain a negative cohesive energy and shifts in band gaps of almost $\frac{1}{2}$ eV.

I. INTRODUCTION

In a recent calculation¹ (hereafter called I), we used a self-consistent warped-muffin-tin potential (SCWMTP) to study the effects of various $x\alpha$ exchange approximations on the energy bands and cohesive energy of γ -Fe. The Kohn-Sham² ($\alpha = \frac{2}{3}$) exchange potential, though better than other exchange potentials, still failed to give cohesion by over $\frac{3}{4}$ Ry per atom. The calculation was made using the modified augmented-plane-wave (APW) method,³ where the basis functions are given by

$$\chi_{\vec{k}}(\vec{r}) = (N\Omega)^{-1/2} \left(e^{i\vec{k}\cdot\vec{r}} - 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^l \sum_j i^l e^{i\vec{k}\cdot\vec{R}_j} \right. \\ \times j_l(Kr_j) - \frac{f_l(r_j)j_l(Kr_0)}{f_l(r_0)} \\ \left. \times Y_{lm}^*(\hat{K}) Y_{lm}(\hat{r}_j) \Theta(r_0 - r_j) \right), \quad (1)$$

where N is the number of unit cells of volume Ω , the f_l are solutions of the radial Schrödinger equation within the inscribed sphere of radius r_0 , the j_l are spherical Bessel functions, $\vec{r}_j = \vec{r} - \vec{R}_j$, with \vec{R}_j a lattice vector, Θ is a unit step function, and the Y_{lm} are spherical harmonics. $\chi_{\vec{k}}(\vec{r})$ differs from the ordinary APW basis function only in that l is summed from 0 to 2 rather than to ∞ . The wave function for a state in the n th band at the point \vec{k} in the Brillouin zone is then

$$\varphi_{n\vec{k}}(\vec{r}) = \sum_{\vec{G}} a_{n\vec{k}\vec{G}} \chi_{\vec{k}\vec{G}}, \quad (2)$$

where the sum is over all reciprocal-lattice vectors \vec{G} . The total $3d$, $4s$, $4p$ charge density may be written

$$\rho(\vec{r}) = \frac{1}{32} \sum_{n,\vec{k}}^{256} |\varphi_{n\vec{k}}(\vec{r})|^2 \\ = \rho_{in}(\vec{r}) + \rho(0) + \sum_{\vec{G}}' \rho(\vec{G}) e^{i\vec{G}\cdot\vec{r}}, \quad (3)$$

where $\rho(0)$ and $\rho(\vec{G})$ are due to plane-wave-plane-wave products in the square of $\varphi_{n\vec{k}}$, and $\rho_{in}(\vec{r})$,

which vanishes outside the inscribed spheres, includes everything else. The sum over the lowest 256 states in the 64-point sample of the Brillouin zone is discussed in I.

In Sec. II we discuss how a self-consistent muffin-tin potential (SCMTP) is ordinarily obtained from (3) in standard APW calculations, how in I we obtained a SCWMTP for use in our modified APW calculation by making a simple generalization of the SCMTP, and finally we describe a new SCWMTP which is more akin to the true crystal potential. We then compare the cohesive energy and energy bands calculated from the two SCWMTP's.

II. SCWMTP

The SCMTP is usually obtained^{4,5} by first taking a spherical average of (3) for $r < r_0$,

$$\bar{\rho}(r) = \bar{\rho}_{in}(r) + \rho(0) + \sum_{\vec{G}}' \rho(\vec{G}) j_0(Gr), \quad (4)$$

and then assuming the remaining charge z is distributed with constant density z/Ω_0 in the interstitial region where $\Omega_0 = \Omega - \Omega_i$ and $\Omega_i = \frac{4}{3}\pi r_0^3$ is the volume of the inscribed sphere. One may calculate z by noting that the last term of (3) has a space average of zero; therefore its contribution to z must be equal and opposite to its contribution to the total charge within the inscribed sphere. Thus

$$z = \rho(0)\Omega_0 - \Delta z, \quad (5)$$

where

$$\Delta z = 4\pi \sum_{\vec{G}}' \int_0^{r_0} \rho(\vec{G}) j_0(Gr) r^2 dr \\ = 4\pi r_0^2 \sum_{\vec{G}}' \rho(\vec{G}) j_1(Gr_0)/G. \quad (6)$$

Note that in the ordinary APW expansion, the spherical Bessel functions exactly cancel the $e^{i\vec{k}\cdot\vec{r}}$ within the inscribed sphere in Eq. (1); therefore the expansion of $\bar{\rho}(r)$ into three terms in Eq. (4) may seem artificial to some practitioners of the APW method. We hope to demonstrate that it is not, but in any event our $\bar{\rho}_{in}(r)$ will contain terms to exactly cancel the $\rho(0)$ and $\rho(\vec{G})$ terms

(in the APW case) so that $\bar{\rho}(r)$ will contain contributions from the radial functions $f_l(r)$ only.

From the charge density distribution $\bar{\rho}(r)$ within the inscribed sphere and z/Ω_0 outside, it is a straightforward matter to calculate the spherically averaged⁶ potential inside the inscribed spheres. In addition, in the APW SCMTP method one needs an *average* value of the potential outside the inscribed spheres, which may be calculated by the method of Slater and DeCicco.⁷ The SCWMTP modified APW calculation requires a spherically averaged potential within the inscribed sphere but uses the exact potential outside. (This exact potential in the interstitial region enters the calculation only through Fourier transforms of the entire crystal potential.) Therefore in I we calculated the energy bands of γ -Fe using exactly the same charge density distribution described above for ordinary APW calculations and exactly the same spherically averaged potential within the inscribed sphere, but the potential in the constant-charge-density interstitial region was not approximated by a constant.

The greatest shortcoming of the SCWMTP described in the preceding paragraph is its neglect of the variation of the charge density in the interstitial region. This has a strong effect on the Coulomb potential inside the inscribed sphere as well as in the interstitial region. Therefore we have recalculated the cohesive energy and energy bands of γ -Fe using

$$\bar{\rho}'(r) = \bar{\rho}_{\text{in}}(r) + \rho(0), \quad (7)$$

$$z' = \rho(0)\Omega_0, \quad (8)$$

$$\rho'_G(\vec{r}) = \sum_{\vec{G}} \rho(\vec{G}) e^{i\vec{G}\cdot\vec{r}}, \quad (9)$$

where the primes are to distinguish the new SCWMTP calculation from the old, and where $\bar{\rho}'(r)$ and z' have the same meaning as $\bar{\rho}(r)$ and z , i. e., a spherically averaged charge density within the inscribed sphere and a charge distributed with constant density in the interstitial region. In addition, we now have $\rho'_G(\vec{r})$ existing throughout the crystal, which yields a Coulomb potential

$$V'_G(\vec{r}) = 8\pi \sum_{\vec{G}} G^{-2} \rho(\vec{G}) e^{i\vec{G}\cdot\vec{r}} \quad (10)$$

whose spherical average

$$V'_G(r) = 8\pi \sum_{\vec{G}} G^{-2} j_0(Gr) \quad (11)$$

replaces the contribution of the last term in Eq. (4) to the potential within the inscribed sphere. In the Appendix we calculate the difference between the spherical averages of the old and new potentials within the inscribed spheres.

The exchange potential was calculated using the old method. Because the Kohn-Sham exchange is proportional to $\rho^{1/3}(\vec{r})$, the superposition theorem does not hold and within the inscribed sphere it

must be calculated from $\bar{\rho}(r)$ of Eq. (4). While it would have been preferable to calculate it in the interstitial region using the exact charge density, it would be very tedious and the error made by treating the interstitial charge as constant introduces a much smaller error in the exchange potential than in the Coulomb potential, for the following two reasons. In the first place, the charge density in the interstitial region does not affect the exchange potential in the inscribed sphere; secondly, the cube root makes the variation of the exchange potential in the interstitial region much less than the variation of the charge density.

In Table I we compare energy levels at points throughout the Brillouin zone for the two calculations. According to the results of the Appendix we expect the new calculation to yield higher one-electron energies, and indeed we find them to average 0.1 Ry higher throughout the Brillouin zone. More important, we find relative shifts of up to 0.0335 Ry between various levels. (Note, however, that the same 256 levels remain below the Fermi surface in the charge density sampling.) The binding energy, calculated from Eq. (I.17), is compared in Table II. We note that the binding energy is a full Ry more negative for the new potential, yielding a negative cohesive energy, whereas for the old SCWMTP the cohesive energy was positive. It is the Madelung terms in (I.17) which yield the extra negative binding energy. Because of the larger negative charge z' in the interstitial region (see Table II) the potential is more repulsive for electrons within the inscribed sphere, but this is dominated by the fact that the same potential is more attractive for the atomic nucleus.

It is interesting to note that standard APW calculations have given good results for the binding energy of Cs⁸ and Al.⁴ This leads us to speculate that in free-electron metals the interstitial charge density is sufficiently constant to justify a SCMTP APW calculation but that for the transition metals the variation of the interstitial charge density must explicitly be taken into account in a modified APW SCWMTP calculation.

APPENDIX

We here calculate the differences between the inscribed-sphere spherical averages of the old and new SCWMTP's (assuming, of course, that they are calculated from the same charge density). First, we have an extra constant density $\Delta z/\Omega_0$ in the interstitial region for the new potential, where $\Delta z = z' - z$ (see Table II) is the contribution of $\sum_{\vec{G}} \rho(\vec{G}) e^{i\vec{G}\cdot\vec{r}}$ to the spherically averaged charge density in the old potential. We calculate the contribution of Δz to the potential by taking a constant charge density $\Delta z/\Omega_0$ existing everywhere plus inscribed spheres of charge density $-\Delta z/\Omega_0$. The

TABLE I. Energy levels for various states (in Ry) calculated using the old and new SCWMTP and their shifts relative to the $\Gamma_{25'}$ level. The number preceding a given state is the weighting of its contribution to the self-consistent charge density.

State	Old	New	Shift
1 Γ_1	0.0827	0.1814	0.0014
3 $\Gamma_{25'}$	0.5692	0.6665	0
2 Γ_{12}	0.6582	0.7593	0.0038
3 X_1	0.3703	0.4837	0.0161
3 X_3	0.4158	0.5121	-0.0010
X_2	0.7195	0.8249	0.0081
X_5	0.7385	0.8443	0.0085
X_4	0.8621	0.9420	-0.0174
4 L_1	0.3659	0.4567	-0.0065
8 L_3	0.5624	0.6616	0.0019
L_3	0.7217	0.8271	0.0081
L_2'	0.6727	0.7852	0.0152
6 Δ_1	0.2789	0.3806	0.0044
6 Δ_2'	0.4871	0.5834	-0.0010
6 Δ_1	0.6015	0.7011	0.0023
12 Δ_5	0.6390	0.7389	0.0026
Δ_2	0.6879	0.7908	0.0056
12 Σ_1	0.4122	0.5099	0.0004
12 Σ_3	0.5088	0.6058	-0.0003
12 Σ_4	0.5291	0.6351	0.0087
12 Σ_4	0.6199	0.7230	0.0058
2 Σ_2	0.6589	0.7605	0.0043
Σ_1	0.8300	0.9340	0.0067
6 W_2'	0.4409	0.5554	0.0172
12 W_3	0.5078	0.6045	-0.0006
6 W_1	0.6506	0.7538	0.0059
W_1'	0.7390	0.8449	0.0086
W_3	1.2603	1.3458	-0.0118
8 Λ_1	0.2354	0.3330	0.0003
8 Λ_1	0.5352	0.6339	0.0014
16 Λ_3	0.5843	0.6830	0.0014
Λ_3	0.6668	0.7696	0.0055
24 E_1	0.4211	0.5221	0.0037
24 E_1	0.4716	0.5780	0.0091
24 E_1	0.5635	0.6598	-0.0010
24 E_2	0.6362	0.7383	0.0048
E_2	0.7270	0.8325	0.0082
E_1	0.9021	1.0127	0.0133
K_1	0.4271	0.5345	0.0101
K_1	0.4531	0.5559	0.0055
K_3	0.5861	0.6835	0.0001
K_4	0.6711	0.7754	0.0070
K_2	0.7209	0.8220	0.0038
K_3	1.1243	1.2126	-0.0090
K_1	1.2337	1.3332	0.0022

former (together with $\Delta z/\Omega_0$ protons on each lattice site) yields a spherically averaged Madelung potential^{1,9}

$$\delta V_{\text{Mad}} = \frac{3.58344}{r_{\text{ws}}} \frac{\Delta z \Omega}{\Omega_0} - \frac{4\pi}{3} \frac{\Delta z}{\Omega_0} r^2, \quad (\text{A1})$$

where $r_{\text{ws}} = (3\Omega/4\pi)^{1/3}$ is the Wigner-Seitz radius, Ω is the unit-cell volume, Ω_0 is the interstitial volume, and Δz is measured in units of electrons

per atom. The potential due to a sphere of constant charge density $-\Delta z/\Omega_0$ is (within the inscribed sphere)

$$\delta V_{\text{sphere}} = - \left(\frac{3}{r_0} - \frac{r^2}{r_0^3} \right) \frac{\Delta z \Omega_i}{\Omega_0}. \quad (\text{A2})$$

The potential due to other spheres when combined with $-\Delta z \Omega_i/\Omega_0$ protons vanishes. Using $\Omega_i = \frac{4}{3}\pi r_0^3$ and adding (A1) and (A2), we obtain

$$\delta V_{\Delta z} = \frac{3.58344}{r_{\text{ws}}} \frac{\Delta z \Omega}{\Omega_0} - 4\pi r_0^2 \frac{\Delta z}{\Omega_0}. \quad (\text{A3})$$

A second difference in the spherically averaged potential is the difference between $V_G(r)$, the contribution of the last term in Eq. (4), and $V'_G(r)$ of Eq. (11). We have

$$\begin{aligned} V_G(r) &= 8\pi \sum'_{\vec{G}} \rho(\vec{G}) [(1/r) \int_0^r j_0(Gr') r'^2 dr' \\ &\quad + \int_r^{r_0} j_0(Gr') r' dr'] \\ &= 8\pi \sum'_{\vec{G}} \rho(\vec{G}) G^{-2} [j_0(Gr) - \cos Gr_0], \quad (\text{A4}) \end{aligned}$$

and on subtracting (A4) from (11) we obtain

$$\delta V_G(r) = 8\pi \sum'_{\vec{G}} \rho(\vec{G}) G^{-2} \cos Gr_0. \quad (\text{A5})$$

Thus the total change in the spherically averaged potential within the inscribed sphere is a constant (independent of r),

$$\begin{aligned} \delta V(r) &= \frac{3.58344}{r_{\text{ws}}} \frac{\Delta z \Omega}{\Omega_0} - 4\pi r_0^2 \frac{\Delta z}{\Omega_0} \\ &\quad + 8\pi \sum'_{\vec{G}} \rho(\vec{G}) G^{-2} \cos Gr_0. \quad (\text{A6}) \end{aligned}$$

Using that for a fcc lattice $r_{\text{ws}} = (3\Omega/4\pi)^{1/3}$, $\Omega = \frac{1}{4}a^3$, and if the inscribed spheres touch, $r_0^2 = \frac{1}{8}a^2$, we can rewrite (A6) as

$$\begin{aligned} \delta V(r) &= (\Delta z a^2 / 2\Omega_0) [3.58344 (\frac{2}{3}\pi)^{1/3} - \pi] \\ &\quad + 8\pi \sum'_{\vec{G}} \rho(\vec{G}) G^{-2} \cos Gr_0. \quad (\text{A7}) \end{aligned}$$

Although (A7) is valid only when the old and new potentials are calculated from the same charge density, we can estimate the first term by taking

TABLE II. Total charge (in electrons per atom) in the interstitial region and binding energy and cohesive energy (in Ry per atom) obtained by subtracting an ionization energy of -2517.788 Ry from the binding energy for the old and new SCWMTP calculations.

	Old	New
z, z'	0.819	1.035
Binding	-2517.005	-2518.018
Cohesive	0.783	-0.275

$\Delta z = z' - z$ from Table II. (Note that z and z' are actually calculated from different self-consistent charge densities.) The first term gives $\delta V(r) = 0.0619$ Ry. The second term is small because the sign of $\rho(\vec{G})$ and $\cos Gr$ is different for different G 's and in fact the sign of the second term is

positive when the old charge density is used and negative when the new charge density is used. Because from this estimate δV is positive, we expect the one-electron energies of the new calculation to be higher than those of the old calculation as Table I confirms.

¹R. Shurtleff and L. Kleinman, Phys. Rev. B 3, 2418 (1971).

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

³L. Kleinman and R. Shurtleff, Phys. Rev. 188, 1111 (1969).

⁴M. Ross and K. W. Johnson, Phys. Rev. B 2, 4709 (1970).

⁵J. B. Conklin (private communication).

⁶Note that the constant charge density outside the inscribed spheres yields a nonspherical potential inside.

⁷J. C. Slater and P. DeCicco, MIT Solid State and Molecular Theory Group Quarterly Progress Report No. 50, 1963, p. 46 (unpublished).

⁸F. W. Averill (unpublished).

⁹L. Kleinman, Phys. Rev. 146, 472 (1966).

Lattice Spacings and Compressibilities vs Pauling Radii and Valencies

A. Meyer, I. H. Umar,*† and W. H. Young‡

Department of Physics, Northern Illinois University, DeKalb, Illinois 60115

(Received 10 May 1971)

The lattice spacings and compressibilities of the nontransition-elemental solids are calculated using Ashcroft pseudopotentials to describe the cores and the von Weizsacker method to describe the valence electrons. The observed correlations of these quantities with the Pauling radii and the valencies are thereby obtained.

I. INTRODUCTION

The success of the pseudopotential method in the theory of metals is now established^{1,2} and it would appear to be an appropriate time to investigate whether the method might be adapted to other systems. We have in mind, in particular, applications to molecular chemistry, a suggestion which has also been made by Harrison.³ The aspect of the standard pseudopotential technique for metals which cannot be taken over into other problems is the method of linear dielectric screening by the valence electrons, which depends on there being a zeroth-order description in terms of plane waves.

In an earlier paper⁴ it was suggested that a Thomas-Fermi (TF) type of description of the valence electrons might be a suitable alternative. Indeed, conversely, the pseudopotential description might be regarded as offering further scope for the extension of TF-like methods which often experience difficulties in the very regions, the cores, which are eliminated on using pseudopotentials.

It is well-known, however, that the TF method alone cannot produce a stable lattice. For this reason, we now generalize the previous work and show that a generalized TF method, namely, the Thomas-Fermi-Dirac-von Weizsacker (TFDW)

description will give accurate interatomic spacings and compressibilities. In fact, it is probably fair to say that the average accuracy achieved is higher than in any other calculation of pseudopotential type.³⁻⁷

II. GENERAL THEORY

In this work we will be interested in describing the total energy E of the system as a functional of the particle density $n(\vec{r})$, the fundamental status of this viewpoint having been discussed by Kohn and coworkers.^{8,9} Let us write

$$E = \int f(n) d\tau - \frac{1}{2} e \int n V_e d\tau + U_{ii} \quad , \quad (2.1)$$

where $e = |e|$ is the size of the electronic charge,

$$V_e = -e \int \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} d\tau' \quad (2.2)$$

is the electrostatic potential resulting from the electron distribution, and U_{ii} represents the Coulombic ion-ion contribution. Specific forms will be taken for f later. The Euler equation for (2.1) reads

$$\frac{\delta f}{\delta n} - e(V_e - V_0) = 0 \quad , \quad (2.3)$$

where V_0 is a Lagrange multiplier arising from