UNIVERSAL MODEL POTENTIAL IN THE AUGMENTED-PLANE-WAVE METHOD

By

R. GÁSPÁR and GY. BÁRDOS

INSTITUTE OF THEORETICAL PHYSICS, KOSSUTH LAJOS UNIVERSITY, DEBRECEN, HUNGARY

(Received 3. II. 1981)

The usefulness of a universal model potential suggested by one of the authors has been investigated in the augmented-plane-wave calculations of the electronic structure of various metals. Results of calculations based on universal model potential are compared with results calculated on the basis of self-consistent-field atomic potentials, and with the free electron model values.

Introduction

In consequence of its simplicity and its analytical form the universal model potential (UMP) suggested by one of the authors [1] may be applied well to calculations based on crystal potentials formed from spherically symmetric atomic potentials. The UMP is a simple analytical function and it depends on spatial coordinates and on atomic numbers only. The UMP differs more or less from more exact self-consistent-field (SCF) atomic potentials, and this difference modifies the results of calculations obtained with the SCF atomic potentials. In the different further applications of the UMP it is useful to know how large a difference may result with respect to the results of calculations based on SCF atomic potential. The calculations presented here by the augmented-plane-wave (APW) method seem to be suitable for the estimation of this difference.

The APW method and the universal potential

The APW method of calculating electronic energy bands is based on the independent electron model of solids. The characteristic feature of the APW method is the subdivision of the crystal into different separated space regions and the assumption of a different form for the crystal potential and different expansion functions for the electron wave functions in these regions. The crystal potential is approximated by a muffin-tin form, which is spherically symmetrical within spheres surrounding each of the atoms in the crystal lattice and constant in the region between the spheres. Within each sphere

the electronic wave functions are expanded in terms of products of radial wave functions and spherical harmonics. In the regions between the spheres the expansion is in terms of plane waves. The expansion coefficients are to be determined on the one hand variationally, on the other hand from the condition of continuity of the wave functions on the spherical surfaces.

The details of calculating the energy eigenvalues using the APW method will not be reproduced here. LOUCKS has given a detailed discussion of the method of computation [2].

The APW matrix elements are

$$M^{ij} = \Omega \left(k_j^2 - E\right) \delta_{ij} - 4\pi \sum_{\nu} S_{\nu}^2 e^{i\mathbf{k}_{ij}\mathbf{r}_\nu} G_{\nu}^{ij} \, ,$$

where the Ω is the volume of the unit cell. The k_j is magnitude of

$$\mathbf{k}_j = \mathbf{k}_j + \mathbf{g}_j \, .$$

$\mathbf{k}$ is the wave vector specifying the state for which the energy eigenvalues are to be calculated. $\mathbf{g}_j$ is the reciprocal lattice vector and

$$\mathbf{k}_{ij} = \mathbf{k}_j - \mathbf{k}_i \, .$$

The $\mathbf{r}_\nu$ is the position of the centre of the ν-th APW sphere in the unit cell, and S_ν is the radius of the ν-th APW sphere. The

$$G_{\nu}^{ij} = (k_j^2 - E) J_1(k_{ij} S_\nu)/k_{ij} - \sum_{l=}^{\infty} (2l+1) P_l \left(\frac{\mathbf{k}_i \mathbf{k}_j}{k_i k_j}\right) J_l(k_i S_\nu) \times$$

$$\times \, J_l(k_j S_\nu) \left[\frac{R_l'(S_\nu, E)}{R_l(S_\nu, E)} - \frac{k_i J_l'(k_j S_\nu)}{J_l(k_j S_\nu)} \right],$$

where J_l is a spherical Bessel function of order l, and P_l is the Legendre polynomial of order l. The

$$\frac{R_l'(S_\nu, E)}{R_l(S_\nu, E)}$$

are the logarithmic derivatives, $R_l(r, E)$ satisfies the radial Schrödinger equation:

$$-\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr}\right) + \left[\frac{l(l+1)}{r^2} + V_\nu(r)\right] R = ER \, ,$$

where $V_\nu(r)$ is the spherically symmetric potential inside the ν-th sphere.

The crystal potential which has been observed in this article, determines the matrix elements through the logarithmic derivatives. Therefore we concentrate on the properties of the logarithmic derivatives in this paper.

If the $V_\nu(r) = 0$, as in the free-electron model, the logarithmic derivatives

$$\frac{R_l'(S_\nu, E)}{R_l(S_\nu, E)} = \frac{\sqrt{E}\, J_l'(\sqrt{E}\, S_\nu)}{J_l(\sqrt{E}\, S_\nu)}$$

are the functions of logarithmic derivatives of the spherical Bessel functions. The APW matrix elements and so the secular determinant is zero if $k_j^2 = E$, as has been expected in the case of the free-electron model.

The muffin-tin potential has been obtained as a superposition of atomic potentials. In the method suggested by MATTHEISS [3] the Coulomb and exchange contributions to the muffin-tin potential are treated separately. The Coulomb part is obtained from a direct superposition of the Coulomb potentials of the central and neighbouring atoms. The charge density obtained from a similar superposition of the atomic charge densities, and the exchange part is calculated using the free-electron exchange approximation.

The Coulomb part of UMP in rydbergs

$$V_c(r) = \frac{2Z}{r}\, \frac{e^{-\lambda_0 x}}{1 + A_0 x}\,,$$

where Z is the atomic number, r is the distance of the electron from the nucleus. The constants of the equation are

$$\lambda_0 = 0.1837, \quad A_0 = 1.05$$

and the scaled variable x is defined by the relations

$$x = \frac{r}{\mu}\,, \quad \mu = \frac{0.88534137}{Z^{1/3}}\, a_0\,,$$

where a_0 is the first Bohr radius in the H atom.

The atomic charge density in the UMP

$$\varrho = Z^2 \left(\frac{Ce^{-\alpha x}}{1 + Ax}\right)^3,$$

where the constants are given by

$$C = 3.1\, a_0^{-1}, \quad \alpha = 0.04, \quad A = 9.0\,.$$

The potential of the exchange energy by the $X\alpha$ method in rydbergs is

$$V_x(r) = -6\, \alpha \left(\frac{3}{8\pi}\, \varrho(r)\right)^{1/3},$$

where $\varrho(r)$ is the charge density obtained from the superposition of the atomic charge densities of UMP form and α is a parameter. Sensitivity of logarithmic derivatives to changes of the exchange potential was observed by changing the α parameter.

Results and discussion

The results obtained with the UMP are compared with results based on SCF atomic potentials. The Coulomb, exchange and crystal potential for the hexagonal-close-packed beryllium, given by TERRELL [4] on the basis of SCF atomic-beryllium potentials are shown in Figs. 1—3 together with the Coulomb and exchange parts, and the crystal potential of the UMP (in the case $\alpha = 1$, $\alpha = 2/3$). Qualitatively the same results have been found for the
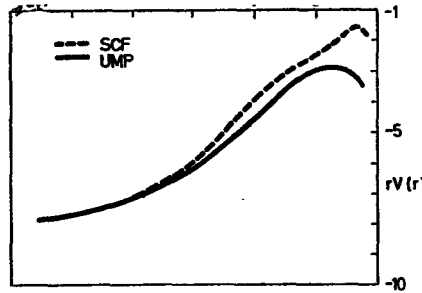
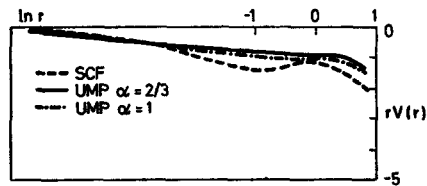*Fig. 1.* The Coulomb potential for beryllium in rydbergs

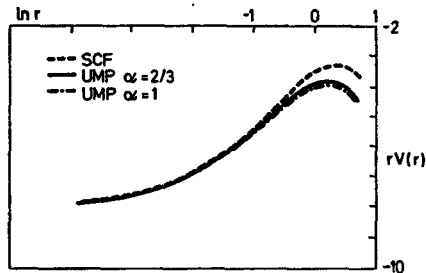*Fig. 2.* The exchange potential for beryllium in rydbergs

Fig. 3. The crystal potential for beryllium in rydbergs

Table I

The average values of crystal potentials for the
metals Be, Cu and Ag (rydbergs)

V_{AVG}	Be	Cu	Ag
SCF	−1.700	−0.939	−0.370
UMP ($\alpha = 2/3$)	−2.150	−2.069	−0.660
UMP ($\alpha = 1$)	−2.233	−2.177	—

metals zirconium and copper, too. The considerable differences present both in the Coulomb part and in the exchange part of the potential largely compensate in the crystal potential.

The universal model crystal potential is more negative, than that based on the SCF calculations. This may be seen from the average values of the potentials for the metals beryllium, copper and silver, too, which are given in Table I.

In the Figs. 4 and 5 are shown the logarithmic derivatives (at the radius of the APW sphere) as a function of energy for two nearly free-electron metals,
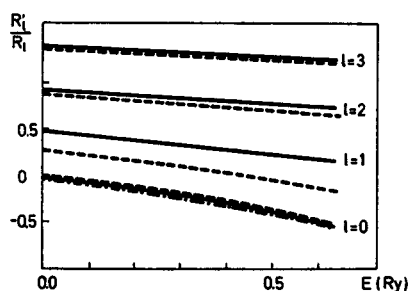

Fig. 4. Logarithmic derivatives (at APW sphere radius) as a function of energy for beryllium —·—·—·— SCF after J. H. TERRELL [4] in the case $l = 0$, ———— free-electron model, · · · · · based on UMP $\alpha = 2/3$ and SCF after J. H. TERRELL, in the case $l = 1$
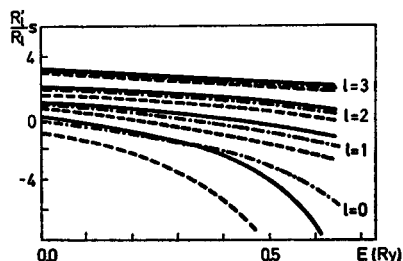

Fig. 5. Logarithmic derivatives (at APW sphere radius) as a function of energy for sodium. —·—·—·— SCF after J. C. SLATER [7], ———— free-electron model, - - - - based on UMP $\alpha = 2/3$

for the beryllium and sodium. Logarithmic derivatives as a function of the energy comparing with the logarithmic derivatives of the free-electron mode show that these metals are nearly free-electron crystals.

In contrast to this we show in Fig. 6 the corresponding curve for zirconium in the case $l = 2$. For the d electrons, $l = 2$, there is no agreement at all between the actual curve and that for the free-electron model. As a consequence of this, the free-electron approximation is entirely erroneous for zirconium, as for other transition elements, which have partially filled d shells. The energy bands of these transition elements depart radically from the free-electron results.

The same results are given for the noble metal copper, logarithmic derivatives of which are seen in Fig. 7. Though the agreement between the logarithmic derivatives calculated with UMP and SCF potential is not as good for this metal, as it is for the transition element zirconium. The logarithmic derivatives of the noble metal copper in contrast to the element zirconium, as they are shown in Figs. 8 and 9 are very sensitive to change of the α parameter, that is to small differences of the potential.
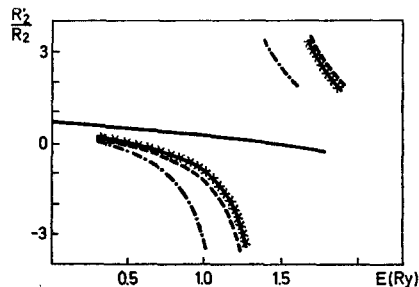

Fig. 6. Logarithmic derivatives (at APW sphere radius) as a function of energy for zirconium in the case $l = 2$. —·—·—·— SFC after T. L. LOUCKS [6], ——— free-electron model, -×-×-×-×- based on UMP $\alpha = 2/3$, - - - - - based on UMP $\alpha = 1$
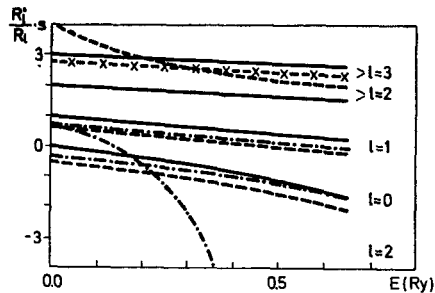

Fig. 7. Logarithmic derivatives (at APW sphere radius) as a function of energy for copper. —·—·—·— SCF after J. C. SLATER [7] in the case $l = 2$, ——— free-electron model, - - - - based on UMP $\alpha = 2/3$, -×-×-×- based on UMP $\alpha = 2/3$ and SCF given by SLATER [7] in the case $l = 3$
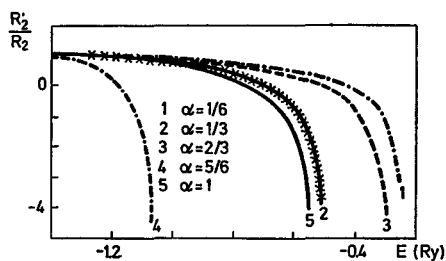
Fig. 8. Logarithmic derivatives (at APW sphere radius) as a function of energy for copper

In Table II the energy eigenvalues are listed for the hexagonal-close-packed beryllium, computed for the free-electron model, with the SCF potential, and with the UMP, respectively. The energy eigenvalues of the free-electron model, and those computed on the basis of the relativistic SCF poten-

Table II

Energy eigenvalues computed by the APW method for beryllium. The energies are in rydbergs.

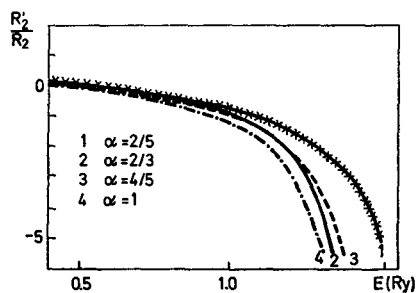| Points of the Brillouin-zone (given in Fig. 11)	Free-electron model	SCF after J. H TERRELL [4]	UMP $\alpha = 2/3$
Γ	0.000	0.000	0.000
	0.861	0.519	0.520
	0.861	0.900	0.905
K	0.941	0.642	0.641
	0.941	0.761	0.757
	1.801	1.304	1.318
	1.801	1.31 3	1.327
M	0.529	0.465	0.465
	0.529	0.605	0.610
	1.390	1.292	1.294
	1.390	1.300	1.300
	1.390	1.096	1.108
A	0.215	0.161	0.157
	1.936	1.595	1.590
H	1.156	0.847	0.847
	1.156	1.257	1.262
	1.156	0.759	0.766

Fig. 9. Logarithmic derivatives (at APW sphere radius) as a function of energy for zirconium

Table III

Energy eigenvalues computed by the APW method for
zirconium. The energies are in rydbergs.

| Points of the Brillouin-zone (given in Fig. 11.)	Free-electron model	SCF after T. L. LOUCKS [6]	UMP $\alpha = 2/3$
Γ	0.000	0.000	0.000
	0.417	0.185	0.230
	1.412	0.437	0.490
K	0.471	0.218	0.274
	0.471	0.289	0.335
	0.471	0.299	0.371
	0.471	0.305	0.376
M	0.353	0.196	0.249
	0.353	0.224	0.274
	0.770	0.376	0.427
A	0.104	0.119	0.133
	0.939	0.426	0.488
	0.939	0.436	0.491
H	0.575	0.275	0.362
	0.575	0.293	0.371
L	0.457	0.180	0.221
	0.457	0.186	0.226
	1.292	0.312	0.404
	1.292	0.316	0.408
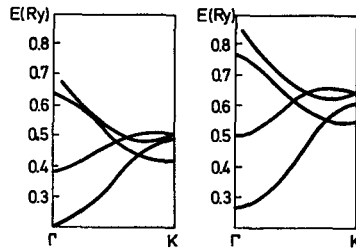
Fig. 10. Energy bands for zirconium along ΓK symmetry directions computed with the SCF given by T. L. LOUCKS and with the UMP
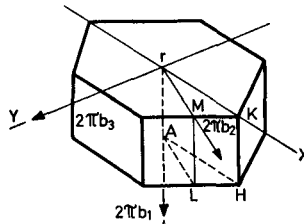

Fig. 11. Half of the Brillouin zone for the exchange-close-packed crystal structure

tial [6] and those of the UMP for hexagonal-close-packed zirconium are listed in Table III. In Fig. 10 energy bands are shown for zirconium along the ΓK symmetry directions of the Brillouin zone, calculated with the relativistic SCF potential and with the UMP. The Brillouin zone of hexagonal-close-packed beryllium and zirconium for which eigenvalues are given, is shown in Fig. 11. The Tables and Fig. 10 show relatively good agreement between calculations for beryllium and zirconium, based on SCF atomic potentials and on the UMP.

REFERENCES

1. R. GÁSPÁR, Acta Phys. Hung., **3**, 263, 1954.
2. T. L. LOUCKS, Augmented Plane Wave Method, W. A. Benjamin, Inc., New York, 1967.
3. L. P. MATTHEISS, Phys. Rev., **133**, A1399, 1964.
4. J. H. TERRELL, Phys. Rev., **149**, 526, 1966.
5. G. A. BURDICK, Phys. Rev., **129**, 138, 1963.
6. T. L. LOUCKS, Phys. Rev., **159**, 544, 1967.
7. J. C. SLATER, Quantum Theory of Molecules and Solids, Vol. 2, McGraw-Hill, New York, 1965.