

## Crystal Potentials in Energy-Band Calculations of Noble Metals

M. M. PANT AND S. K. JOSHI

*Physics Department, University of Roorkee, Roorkee, India*

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The prevalent prescriptions for constructing crystal potentials are used to determine the energy bands for silver. The Kohn-Rostoker method is applied to determine the energy eigenvalues at the symmetry points  $\Gamma$ ,  $X$ , and  $L$  and along the  $\Delta$ ,  $\Lambda$ , and  $\Sigma$  axes. General conclusions with respect to the suitability of a given potential to noble metals are drawn from a comparison of the important energy-level separations and Fermi-surface parameters of copper (from available calculations) and silver (this calculation) with experiment. It is concluded that the most reasonable representation of the crystal potential for noble metals is obtained by a superposition of atomic potentials, with a proper choice of electronic configuration.

### I. INTRODUCTION

THE two techniques commonly used for energy-band calculations of the noble metals are the augmented-plane-wave (APW) method<sup>1,2</sup> and the Green's-function method<sup>3,4</sup> [also called the Kohn-Rostoker (KR) method]. For the noble metals, the distinction between the core and conduction-band states is not quite clear cut, and the orthogonalized-plane-wave (OPW) method is not suitable for calculating their band structures.<sup>5</sup> The Green's-function and APW schemes have been successfully applied to these metals, and both methods are found to yield identical results when the same potential is employed in the calculation.<sup>6</sup> The chief problem in an energy-band calculation is, therefore, the construction of the crystal potential. Even for a self-consistent calculation, a realistic crystal potential is desirable as a starting point.

The purpose of the present work was to examine the various prevalent prescriptions for constructing the crystal potential, and to assess the relevance of these to noble metals by an appeal to experimental facts. Copper has been the subject of several theoretical energy-band calculations that were derived from basic considerations.<sup>6-10</sup> Both the APW and KR methods have been exploited to determine the band structure of copper for several potentials. Results indicate that the band structure is sensitive to the details of the potential. A large amount of information about the band structure of silver has accrued from experiments,<sup>11</sup> and the few theoretical calculations reported for it do not

agree very well with each other.<sup>5,12,13</sup> Since silver is heavier than copper, it provides a more severe test of the crystal potential. At the same time, it is not heavy enough to necessitate relativistic band calculations. For gold, a relativistic calculation would be imperative. It was therefore thought that an investigation of the dependence of the energy bands of silver on the choice of the crystal potential would be illuminating. A comparison of the results for copper and silver with experiment would allow some general conclusions to be drawn with respect to the suitability of a given potential for noble metals. While we do not discuss gold, our conclusions would be of some possible help for a future relativistic band calculation for it.

The KR method was preferred to the APW method in making these calculations for the following reasons.

(1) The secular determinant in the KR method is considerably smaller than that needed in the APW method, and therefore requires less computational effort. Symmetry considerations result in a further reduction—so much so that a  $4 \times 4$  determinant was the largest that had to be evaluated in this investigation.

(2) The other advantage of the KR method is that certain functions of energy and the wave vector, called *structure constants*, depend only on the lattice structure and not on the crystal potential. These can therefore be tabulated once and for all for a given lattice structure. The only potential-dependent functions that enter the secular determinants are the logarithmic derivatives (at the surface of the muffin-tin sphere) of the solutions of the Schrödinger equation with the chosen potential, and these can be obtained by a straightforward numerical integration. This method is therefore particularly suitable for studying the influence of the potential on the energy bands.

We have used the KR method to evaluate the band energies for silver for the various irreducible representations at the symmetry points  $\Gamma$ ,  $X$ , and  $L$  and along the  $\Delta$ ,  $\Lambda$ , and  $\Sigma$  axes. This limited calculation does not allow a determination of the density of states, nor does it give detailed information about the Fermi surface.

<sup>1</sup> J. C. Slater, *Phys. Rev.* **51**, 846 (1937).

<sup>2</sup> T. L. Loucks, *Augmented Plane Wave Method* (W. A. Benjamin, Inc., New York, 1967).

<sup>3</sup> W. Kohn and N. Rostoker, *Phys. Rev.* **94**, 1111 (1954).

<sup>4</sup> F. S. Ham and B. Segall, *Phys. Rev.* **124**, 1786 (1961).

<sup>5</sup> S. Chatterjee and S. K. Sen, *Proc. Phys. Soc. (London)* **87**, 779 (1966).

<sup>6</sup> B. Segall, *Phys. Rev.* **125**, 109 (1962); G. A. Burdick, *ibid.* **129**, 138 (1963).

<sup>7</sup> R. A. Ballinger and C. A. W. Marshall, *Proc. Phys. Soc. (London)* **91**, 203 (1967).

<sup>8</sup> L. F. Mattheiss, *Phys. Rev.* **134**, A970 (1964).

<sup>9</sup> E. C. Snow, *Phys. Rev.* **171**, 785 (1968).

<sup>10</sup> H. L. Davis, J. S. Faulkner, and H. W. Joy, *Phys. Rev.* **167**, 601 (1968).

<sup>11</sup> C. N. Berglund and W. E. Spicer, *Phys. Rev.* **136**, A1044 (1964); B. R. Cooper, H. Ehrenreich, and H. R. Phillip, *ibid.* **138**, A494 (1965).

<sup>12</sup> B. Segall, General Electric Research Laboratory Report No. 61-RL-(2785 G), 1961 (unpublished).

<sup>13</sup> E. C. Snow, *Phys. Rev.* **172**, 708 (1968).

It is, however, sufficient to depict the salient features, such as the widths of the  $sp$  and  $d$  bands, their relative locations, and the Fermi level, which can be compared with optical data. Contact of the Fermi surface at the zone face is investigated, and under certain approximations<sup>6</sup> (which do not involve errors of more than 3–5%), the neck and belly radii can be estimated and compared with experimental results from de Haas–van Alphen (dHvA) or magnetoacoustic measurements.

## II. RESULTS AND DISCUSSION

### A. Gaspar Potential

Gaspar and Ivanecsko<sup>14</sup> have suggested a phenomenological potential of the form

$$V(r) = -\frac{2Z}{r} \frac{e^{-\lambda_0 r}}{1+A_0 r} - \frac{C'e^{-\alpha r}}{1+Ar} f_{\text{ex}},$$

where the first term simulates the Coulomb contribution and the second the exchange. Such a potential (without the  $f_{\text{ex}}$  factor in the second term) has been used for copper by Ballinger and Marshall,<sup>7</sup> who find satisfactory agreement with experiment and other theoretical results when the exchange is reduced to 0.4 of its full value. We have, therefore, inserted a factor  $f_{\text{ex}}$  in the exchange term and computed the energies by varying  $f_{\text{ex}}$  through a range of values. The values of the other parameters used in the calculation for silver are the following:

$$\begin{aligned} \lambda_0 &= 0.74883, & \alpha &= 0.16305, \\ A_0 &= 4.28017, & A &= 36.68715, \\ C' &= 39.75900, & Z &= 47 \end{aligned}$$

The exchange contribution was varied by assigning the values 0.60, 0.80, 1.00, 1.25, 1.50, and 1.70 to  $f_{\text{ex}}$ . It is found that the band structure is represented best when  $f_{\text{ex}}$  is a little greater than 1.50.

The  $L_{2'}-L_1$  gap decreases with increasing  $f_{\text{ex}}$  up to a value near  $f_{\text{ex}}=1.50$ , after which it starts increasing again. The gap is 0.45 Ry for  $f_{\text{ex}}=1.50$ , which is considerably higher than the experimental value of 0.31 Ry. The energy difference  $E_{F-L_{2'}}$ , which locates the high-symmetry point nearest the Fermi level, has been measured by Berglund and Spicer.<sup>11</sup> Our calculations reveal that this gap decreases with increasing  $f_{\text{ex}}$  and attains the value 0.074 Ry at  $f_{\text{ex}}=1.50$ , compared with the experimental value of 0.022 Ry.<sup>11</sup> At  $f_{\text{ex}}=1.70$ , this gap becomes  $-0.0127$  Ry, meaning thereby no contact of the Fermi surface at the zone face. This again suggests a value a little greater than 1.50 for  $f_{\text{ex}}$ .

The results indicate that the Gaspar potential can be stretched to represent the band structure by assigning to the factor  $f_{\text{ex}}$  a value somewhat greater than 1.50, but even then it is in considerable disagreement

with experiment. We believe that if the Gaspar potential is to be used at all in band calculations for the noble metals, merely changing one parameter<sup>7</sup> is not enough. It is likely that variation of more parameters may lessen the discord with experimental results for the band structure of silver.

### B. Atomic Potential

Next we have evaluated the  $E(\mathbf{k})$  for a self-consistent atomic potential of silver derived from the Hartree-Fock-Slater scheme. Such a potential (obtained from the Herman-Skillman program<sup>15</sup>) has already been used in a band-structure calculation of Cu.<sup>7</sup> We find that for silver the results for this potential are surprisingly close to the experimental results. The Fermi surface touches the zone face at  $L$  and  $E_{F-L_{2'}}$  has a value of 0.016 Ry, which is close to the experimental value of 0.022 Ry. The  $L_{2'}-L_1$  gap is 0.267 Ry, compared with the experimental value of 0.31 Ry. The state  $\Gamma_{25'}$  is pulled below  $\Gamma_1$ ; the  $\Gamma_{25'}-\Gamma_1$  gap being  $-0.01$  Ry, which is equal to the value obtained by Snow<sup>13</sup> from a self-consistent APW calculation with a potential constructed by using the full Slater exchange. But the  $d$  bands are pushed below the Fermi level considerably more than predicted by experiments. For copper, on the other hand, Ballinger and Marshall's<sup>7</sup> calculations show that the over-all picture of the energy bands derived from an atomic potential<sup>15</sup> is not satisfactory. The  $d$  bands were found to be too narrow and too low, and the Fermi surface did not touch the Brillouin zone (BZ).

It is clear that the potential experienced by an itinerant electron within the lattice is not quite the same as that felt by an electron in an atom. However, the following considerations indicate that the crystal potential, in some situations, may not be very much different from the atomic potential.

The crystal potential is sometimes regarded as the sum of a Coulomb and an exchange part, both being obtained from free-atom wave functions.<sup>16</sup> The crystal Coulomb potential is built up from an overlap of the atomic Coulomb potentials and the crystal charge density as a spherically symmetric superposition of atomic charge densities. The exchange is taken to be proportional to the cube root of the charge density. The Slater<sup>17</sup> exchange is thought to exaggerate the actual exchange, and various schemes have been suggested to approximate the exchange in a better way.<sup>18</sup> It is just possible that the crystal Coulomb potential plus a reduced Slater exchange derived from the crystal charge density may more or less equal the atomic Coulomb potential plus the full Slater exchange for the

<sup>15</sup> F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall Inc., Englewood Cliffs, N. J., 1963).

<sup>16</sup> L. F. Mattheiss, *Phys. Rev.* **133**, A1399 (1964).

<sup>17</sup> J. C. Slater, *Phys. Rev.* **81**, 385 (1951).

<sup>18</sup> J. E. Robinson, F. Bassani, R. S. Knox, and J. R. Schrieffer, *Phys. Rev. Letters* **9**, 215 (1962); W. Kohn and L. J. Sham, *Phys. Rev.* **140**, A1133 (1965).

<sup>14</sup> R. Gaspar and K. M. Ivanecsko, *Acta Phys. Acad. Sci. Hung.* **6**, 105 (1956).

TABLE I. Important energy-level separations from various calculations on Ag (in Ry).

	$\Gamma_{25'}-\Gamma_1$	$X_5-\Gamma_1$	$X_5-X_1$	$X_{4'}-\Gamma_1$	$E_F-X_5$	$E_F-L_3$	$E_F-L_{2'}$	$L_{2'}-L_1$
Expt.:								
Berglund and Spicer			0.26		0.28	0.28	0.022	0.31
Previous calc.:								
Segall:								
Hartree	0.26	0.40	0.27	0.66	0.14	0.16	0.03	0.40
Hartree-Fock	0.07	0.19	0.24	0.73	0.23	0.29	-0.09	0.20
Snow:								
Slater = 1	-0.011	0.105	0.198	0.665	0.387	0.400	-0.013	not
Slater = $\frac{5}{8}$	0.090	0.221	0.235	0.667	0.290	0.304	0.007	quoted
Present calc.:								
Herman-Skillman potential	-0.010	0.044	0.185	0.662	0.43	0.41	0.016	0.267
Gaspar potential $f_{ex} = 1.50$	0.395	0.567	0.386	0.710	0.035	0.207	0.074	0.446
Overlap of charge densities from a $4d^95s^2$ configuration	0.316	0.434	0.275	0.700	0.131	0.149	0.074	0.42

atomic charge density. Further, a comparison of the Herman-Skillman atomic potential for silver with self-consistent crystal potentials obtained by Snow<sup>13</sup> shows that atomic potential is close to the self-consistent crystal potential using the full Slater exchange. Thus the Herman-Skillman potential approximates well the actual crystal potential for a moderately heavy metal like silver.

### C. Heine Potential

This type of potential is ordinarily used for OPW calculations for simple metals, and the crystal potential is obtained as a sum of several individual contributions of the core and the conduction electrons.<sup>19</sup> The noble metals have been found to exhibit a band structure consisting of a narrow  $d$  band appreciably hybridized with  $sp$  bands. The identification of the core and the conduction states is therefore not simple, and it is believed at the very outset of this study that a potential constructed according to the prescription of Heine, which assumes a sharp distinction between the core and the conduction electrons, is not a satisfactory representation for the noble metals. However, we thought it interesting to study the nature of the results obtained for silver on using such a potential.

The contribution of the ion core to the crystal potential was taken to be the sum of the Coulomb contribution of a  $Ag^+$  ion plus the exchange between its core electrons. The conduction electrons were assumed to be uniformly distributed inside the Wigner-Seitz cell. The exchange and correlation between the core and the conduction electrons is calculated from a screened Slater exchange suggested by Robinson *et al.*<sup>18</sup> This is admittedly an oversimplification of the correlation effects, but has the advantage of being easily amenable to computation.

The results for this potential corroborate our conjecture that such a potential is not suitable for the noble metals. The  $d$  bands are too high and at the point  $X$ , the  $X_5$  state is found to be higher than  $X_{4'}$ . There is a

pronounced discrepancy for the widths of the  $d$  band as given by the energy difference  $X_5-X_1$  which is twice the experimental value.<sup>11</sup> The width of the  $sp$  band as measured by  $X_{4'}-\Gamma_1$  is 0.69 Ry, which is of the same order as obtained from other calculations.

An investigation by Mattheiss<sup>16</sup> of the effect of atomic configuration on the band structure of the transition-metal series (using a different form of the potential) revealed that using atomic wave functions from a configuration containing an additional  $s$  electron and one less  $d$  electron narrows the  $d$  band and pulls it down toward the  $sp$  bands. For silver too, if we assume a smaller number of  $d$  electrons, the potential will become more attractive for  $d$  electrons. This will narrow the  $d$  band and lower it with respect to the  $sp$  band.

### D. Superposed Atomic Potentials

The Gaspar potential can satisfactorily represent the band structure of copper by the mere change of a single parameter, whereas for silver even moderate changes in the exchange term fail to produce good results. The atomic potential, on the other hand, while giving tolerable results for silver, was unsuccessful for copper. The Heine prescription without any contamination by the hybridization effects is unrealistic and untenable for noble metals. It is therefore clear that none of these potentials approximates well the actual lattice potential for the noble metals. In this subsection we discuss a potential that has come to be widely used in energy-band calculations of transition and noble metals.

Reference has been made in Sec. II B to potentials generated from a superposition of atomic potentials.<sup>16</sup> This method does not demand a distinct categorization into core and conduction electrons. Rather, the critical point here is the choice of the atomic charge densities to be used for constructing the crystal potential. This is important because the  $d$  bands have been found to be sensitive to the choice of atomic configuration.<sup>8</sup> Snow *et al.*<sup>20</sup> find for Ni a satisfactory agreement with dHvA

<sup>19</sup> V. Heine, Proc. Roy. Soc. (London) **A240**, 340 (1957); **A240**, 354 (1957); **A240**, 361 (1957).

<sup>20</sup> E. C. Snow, J. T. Waber, and A. C. Switendick, J. Appl. Phys. **37**, 1342 (1966).

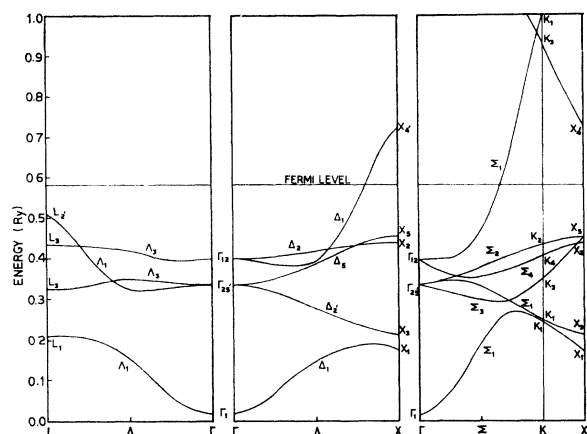


FIG. 1. Energy bands of silver for a potential constructed from overlap of atomic potentials obtained for a  $4d^{10}5s^1$  configuration from wave functions for a  $4d^95s^1$  configuration.

results on assuming an electronic configuration of the type  $3d^{10-x}4s^x$  and assigning to  $x$  a value between 0.5 and 1. Davis *et al.*<sup>10</sup> have studied the effects of changing the atomic wave functions on the band structure of copper. Their findings, in the light of the abundant experimental data for copper, indicate that the potential generated for a  $3d^{10}4s^1$  configuration, by using atomic wave functions<sup>21</sup> for a  $3d^94s^2$  configuration, gave best results. This can be understood because the effective occupation number of orbitals changes on going from a free atom to a crystalline environment, because of the overlap of  $d$  and  $s$  bands in the noble metals. For silver, we have accordingly chosen to calculate the charge density for a  $4d^{10}5s^1$  configuration from atomic wave functions obtained from the Hermann-Skillman program for an assumed  $4d^95s^2$  configuration. The crystal potential is then obtained in the standard way by an overlap of the atomic potentials, through sixth neighbors in the present case. Comparison of results obtained from potentials constructed by using the various prevalent expressions<sup>18</sup> for the exchange potential shows that, for charge densities obtained from this configuration, best results are obtained with the full Slater exchange. Reducing the exchange potential as compared to Slater exchange by any of the proposed schemes has the effect of increasing the discrepancy with experiments.

The widths of the  $sp$  and  $d$  bands for this potential are in good agreement with experiment and with Snow's theoretical results. However, the Fermi level is much lower with respect to the  $d$  bands than predicted by experiment. The  $E_F-L_2$  gap is 0.076 Ry, which is considerably larger than the experimental value of 0.022 Ry. The neck radius is found to be  $0.37k_F$ , compared to Shoenburg's<sup>22</sup> experimental value of  $0.14k_F$ . Here  $k_F$  is the free-electron Fermi-surface radius. Reducing the

<sup>21</sup> R. E. Watson, Phys. Rev. **119**, 1934 (1960).

<sup>22</sup> D. Shoenberg, Phil. Mag. **5**, 105 (1960).

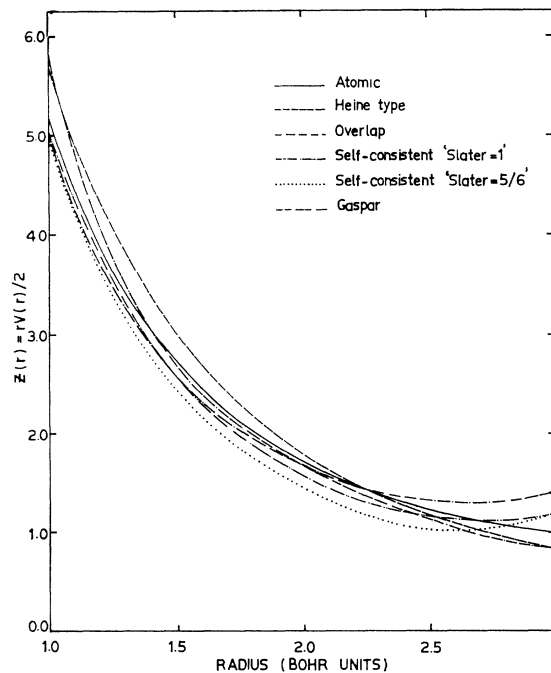


FIG. 2. Charge  $Z(r) = -\frac{1}{2}rV(r)$  for the potentials employed in the calculations for silver and for Snow's self-consistent potentials.

exchange pushes the Fermi level still further upwards. The  $E(\mathbf{k})$  curves for this potential are presented in Fig. 1. Important energy-level separations for the different potentials are compared with experiment and with other theoretical results in Table I.

The "charge"  $Z(r) = -\frac{1}{2}rV(r)$  for the various potentials employed in our calculation for silver is shown in Fig. 2, together with Snow's self-consistent potentials.

### III. CONCLUSION

It is concluded that empirical potentials are too simple to be used with any reasonable success. The agreement with experiments, for the results of the Hermann-Skillman atomic potential, is deemed fortuitous and is not a general feature for all noble metals. The Heine scheme is not appropriate for noble metals, and the evidence seems to add up to a fairly clear preference for a potential constructed à la Mattheiss with a proper choice of electronic configuration.

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