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# Effect of Electronic Correlation on the Energy Bands of Insulating Crystals. Application to Argon†*

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A study has been made of the effect of electronic correlation on the electronic states of insulating solids. This study is based upon a many-body theory first developed by Hedin and used in semiconductors by Brinkman and Goodman. In order to test the theory, band-structure calculations for argon were made using the orthogonalized-plane-wave method. For comparison, calculations were made using a Slater exchange, using a Hartree-Fock exchange, and including correlations at various symmetry points of the first Brillouin zone. In the Hartree-Fock calculation the exchange potential was treated in a nearly exact manner, but no iterations toward self-consistency were performed. Among the most interesting results are as follows: (a) A Hartree-Fock exchange given an energy gap which is too large; (b) a calculation with correlation yields an energy gap within 5% of experiment; (c) correlation has the effect of lowering the band gap by 3.5 eV, a relatively large number, as suggested some time ago by Fowler; (d) the internal structure of the energy bands changes little with different potentials, but the band gap varies considerably as one goes from, e.g., Slater to Hartree-Fock; and (e) the width of the valence bands is relatively large.

## I. INTRODUCTION

In recent years, very significant progress has been made in the experimental measurements in solids of effective masses of holes and electrons and in the determination of energy gaps between bands.[1] These developments lead one to ask how closely ordinary energy-band theory can be expected to be in agreement with experiment. In what we term ordinary energy-band theory,[2] one writes the many-electron wave functions as a single determinant of one-particle Bloch functions $\Psi_{n,\vec{k}}(\vec{r})$ labeled by a band index $n$ and a propagation vector $\vec{k}$, and ideally the one-particle functions would be self-consistent solutions of the Hartree-Fock (HF) equations.[3] Such a self-consistent solution is nearly impossible to carry out because of the great computational difficulties involved. However, there are reasons to believe[4] that even a true solution of the HF equations would not provide satisfactory values for the effective masses and energy gaps in many cases. This is because the one-particle equations, of which the $\Psi_{n,\vec{k}}(\vec{r})$ are solutions, contain none of the dielectric properties of the solid.

One is, therefore, faced with the following two problems: (a) How reliable are the results obtained with the HF equations?; (b) how can we treat correlation effects due to electron-electron interactions and how important are these effects? These questions are the object of the present work.

The system chosen for the calculation is argon. Argon crystallizes into a fcc structure and has a lattice constant of 5.43 Å at 38 °K.[5] There are many reasons why we have chosen argon, among which are the following: (i) It is a relatively simple solid; (ii) there are other theoretical calculations to compare with[6,7]; and (iii) there are some experimental results available.

The method used for the band calculation is the orthogonalized-plane-wave (OPW) method.[8] It is noted that only recently has this method been applied to calculate valence energy bands in the case of insulators.[9–11] In the literature, the use of OPW has been mainly restricted to metals or semiconductors. Our calculation verifies that it is possible to use the OPW method to calculate energy bands and to obtain well-converged energy levels in insulators; thanks also to the large computers available for the calculations.

In recent years, energy-band calculations in insulating solids have become quite common, but, although these calculations are extremely useful from the practical point of view, in the sense that they try to interpret the optical experiments, they do not say very much from the first-principle point of view. This is because virtually all the calculations make some sort of approximations to the exchange potential. However, it has been seen that different methods of approximating the exchange potential can produce widely varying results.[12] Therefore, one can conclude that some of the agreement of such calculations with experiment is merely fortuitous. It is important to investigate this aspect more closely and to try to treat the exchange potential in a way as exact as possible so that one can be confident that the results obtained using the HF equations reflect these equations and not the particular approximations used in treating the exchange.

Much use has been made in the literature of a particular approximation to the exchange potential, that is the Slater approximation,[13] which consists of a local approximation to the nonlocal HF exchange. We will assume the conventional *a priori* position that the Slater approximation lies entirely in the scheme of the HF approximation.

In Sec. II, we present the general concepts of the band theory together with the HF equations and the Slater approximation, and show the numerical results for argon.

The next problem is to include correlation effects. Although we now have a wealth of beautiful theorems, fairly little has been done toward manageable and reliable approximations. One of the biggest steps in this direction has been made by Hedin.[14,15] The result of Hedin's analysis is the introduction of the "Coulomb-hole plus screened exchange" approximation (COHSEX). This approximation has been used by Brinkman and Goodman[16] for the case of valence semiconductors. In Sec. III, we present the result of Hedin's theory following closely Brinkman's notation and analysis. In Sec. IV, we present the results of the effective one-electron equation including correlation, and we briefly present the theory of Haken-Schottky and Fowler[17] concerning electronic polarization in insulators. It is shown that a reasonable qualitative agreement exists between the two theories. In Sec. V, we discuss the results and we compare them with experiment.

## II. VALENCE AND CONDUCTION BANDS

### A. Theory

Let us define

$$\langle x|T|x'\rangle = \delta(x-x')(-\hbar^2\nabla^2/2m) \ ,$$

$$\langle x|V_c|x'\rangle = \delta(x-x')\left(\sum_{\nu}\frac{e^2 Z}{|\vec{r}-\vec{R}_\nu|} + e^2\int\frac{\rho(r'')\,dr''}{|\vec{r}-\vec{r}\,''|}\right) , \qquad (2.1)$$

$$\langle x|V_{\text{ex}}|x'\rangle = -e^2\rho(x,x')/|\vec{r}-\vec{r}\,'| \ ,$$

where

$$\rho(x,x') = \sum_{s}^{N}\varphi_s(x)\,\varphi_s(x') \ ,$$

$$\rho(\vec{r}) = \sum_{\sigma\sigma'}\delta(x-x')\,\rho(\vec{x},\vec{x}\,') \ , \qquad (2.2)$$

$$\delta(x-x') = \delta_{\sigma\sigma'}\,\delta^3(\vec{r}-\vec{r}\,') \ ,$$

$\sigma$ is the spin coordinate, $eZ$ is the nuclear charge, $\vec{R}_\nu$ is the position of the $\nu$th atom, and $\varphi_s$ is a solution of the HF equations (2.3). We can then write the HF equations in the following concise form:

$$(T+V_c+V_{\text{ex}})\,\varphi_i = E_i\,\varphi_i \ . \qquad (2.3)$$

We have already decided to use the OPW method to calculate the valence and the conduction bands. In this method one assumes as a basis set of functions,

$$\varphi_p^\alpha = S_p^\alpha - \textstyle\sum_j \langle\phi_j^\alpha|S_p^\alpha\rangle\,\phi_j^\alpha \ , \qquad (2.4)$$

where $\phi_j^\alpha$ is a symmetrized core eigenfunction and $S_p^\alpha$ is a symmetrized combination of plane waves which have the same kinetic energy, that is,

$$S_p^\alpha = (N\Omega)^{-1/2}\textstyle\sum_j b_{pj}^\alpha \exp(i(\vec{k}+\vec{K}_j)\cdot\vec{r}) . \qquad (2.5)$$

Here, the quantities $b_{pj}^\alpha$ are chosen so that $S_p^\alpha$ transforms according to the $\alpha$ irreducible representation of the group of the wave vector $\vec{k}$, and $N$ represents the number of unit cells of volume $\Omega$. $\vec{K}_j$ is a reciprocal-lattice vector. The wave functions $\varphi_p^\alpha$ so constructed are orthogonal to the core states, but are not mutually orthogonal nor normalized.

A general expression for the valence and conduction wave functions is given by

$$\Psi_{\vec{k},n}^\alpha(\vec{r}) = \textstyle\sum_p d_{p,n}\,\varphi_p^\alpha \ . \qquad (2.6)$$

These functions are now orthogonal and the coefficients $d_{pn}$ are chosen in such a way that they are also normalized.

We also introduce the core projection operator defined as

$$P_c^\alpha = \sum_{nc} P_{nc}^\alpha = \sum_{\vec{k},nc} |\phi_{\vec{k},nc}^\alpha\rangle\langle\phi_{\vec{k},nc}^\alpha| \ , \qquad (2.7)$$

so we can write (2.4) as

$$\varphi_p^\alpha = (1-P_c^\alpha)\,S_p^\alpha \ . \qquad (2.8)$$

If we now substitute (2.6) into (2.3) we get

$$\sum_p d_{p,q}\Big[(T+V_c+V_{\text{ex}})S_p^\alpha - \sum_{nc}E_{nc}^\alpha P_{nc}^\alpha S_p^\alpha - E_q^\alpha S_p^\alpha + E_q^\alpha\sum_{nc}P_{nc}^\alpha S_p^\alpha\Big] = 0 \ , \qquad (2.9)$$

where we have used the equation

$$(T+V_c+V_{\text{ex}})\,\phi_{\vec{k},nc}^\alpha = E_{nc}^\alpha\,\phi_{\vec{k},nc}^\alpha \ . \qquad (2.10)$$

Rearranging the terms of Eq. (2.9) we have

$$\sum_p d_{p,q}\left((T+V_c+V_{\text{ex}})S_p^\alpha + \sum_{nc}(E_q^\alpha - E_{nc}^\alpha)P_{nc}S_p^\alpha - E_q^\alpha S_p^\alpha\right) = 0 . \qquad (2.11)$$

To solve the above equation we can use three different methods; a perturbation approach,[18] a pseudopotential one,[19,20] and a direct one.

The method we shall use consists of a direct diagonalization of the secular matrix $M$, whose elements are

$$M_{pp'} = \langle S_{p'}^\alpha|T+V_c+V_{\text{ex}}|S_p^\alpha\rangle - \sum_{nc}E_{nc}^\alpha\langle p'|P_{nc}^\alpha|p\rangle$$

$$-E\Big(\delta_{p,p'}-\sum_{nc}\langle p'|P^{\alpha}_{nc}|p\rangle\Big) \quad . \qquad (2.12)$$

The problem of diagonalizing such a matrix is not an easy one. The set of basis functions includes, in general, a very large number of plane waves in order to obtain accurate eigenfunctions and eigenvalues. In our case, they can be as high as 50 × 50. The standard approach to diagonalization would be to assume a small basis set and solve the corresponding matrix, then to add other sets and solve again. The set of eigenvalues and eigenvectors obtained in the latter case will be different than in the former. The process is stopped when adding further sets, the energy eigenvalues change within a small established range. We then say that the convergence criterion has been satisfied.

The process of diagonalizing the OPW matrix is straightforward, but evaluation of the matrix elements involved is somewhat laborious. In order to make the argument complete we will write explicitly the matrix elements involved. These are the orthogonality matrix elements and the Fourier transform of the potential. The orthogonality elements are calculated by expanding the plane waves $S^{\alpha}_{p}$ in spherical harmonics. We get

$$(S^{\alpha}_{p'}\,|\,\phi^{\alpha}_{nl},\,S^{\alpha}_{p})=\textstyle\sum_i\sum_j b^{\alpha *}_{p'i}\,b^{\alpha}_{pj}\,A^{*}_{nl}(|\vec{k}+\vec{K}_i|)$$

$$\times A_{nl}(|\vec{k}+\vec{K}_j|)\,P_l(\cos\theta) \quad , \qquad (2.13)$$

where

$$A_{nl}(|\vec{k}+\vec{K}_j|)=i^{l}\,[4\pi(2l+1)/\Omega]^{1/2}$$

$$\times\int_0^{\infty} r j_l(|\vec{k}+\vec{K}_j|r)\,P_{nl}(r)\,dr \,, \qquad (2.14)$$

$$\cos\theta=(\vec{k}+\vec{K}_i)\cdot(\vec{k}+\vec{K}_j)/|\vec{k}+\vec{K}_i|\;|\vec{k}+\vec{K}_j| \quad . \qquad (2.15)$$

Now we have to consider the problem of the potential. We have already seen that our potential is the sum of a Coulomb part and of an exchange part. For the Coulomb part, which is local, we can calculate the Fourier transform according to

$$V_c(K)=(N\Omega)^{-1}\int e^{i\vec{K}\cdot\vec{r}}\,V_c(\vec{r})\,d\vec{r}, \qquad (2.16)$$

$$V_cK=(4\pi/K\Omega)\int_0^{\infty} r\sin(Kr)\,V_c(r)\,dr \quad , \qquad (2.17)$$

where $\Omega$ is the volume of the unit cell. $V(K)$ depends only on the magnitude of $K$; $\vec{K}$ being equal to $\vec{K}_i-\vec{K}_j$. $V_c(0)$ is chosen according to

$$V_c(0)=(4\pi/\Omega)\int_0^{\infty} r^2\,V_c(r)\,dr \quad . \qquad (2.18)$$

The exchange part needs special treatment. In the case in which we use the Slater approximation, the problem presents no difficulty because the exchange is now local, and so we can treat it together with the Coulomb part, i.e.,

$$V(r)=V_c(r)+V_{\rm ex}(r) \quad . \qquad (2.19)$$

The Fourier transform of $V$ is defined in complete analogy to the case of the Coulomb part described before.

However, the exchange potential is, in general, not local. Let us write the exchange operator in the form

$$\langle\vec{x}\,|\,V_{\rm ex}\,|\,\varphi(x')\rangle=-e^2\int\sum_{\vec{k},n}\frac{\varphi_{\vec{k},n}(\vec{x})\,\varphi_{\vec{k}n}(x')\,\varphi(x')}{|\vec{r}-\vec{r}'|}\,dx \quad . \qquad (2.20)$$

In the summation, only one member with a spin-up spin-down pair of orbitals is included. In the ground state, only filled subshells occur. In this event, the Bloch and the Wannier representations[21] are equivalent. Therefore, if we assume that the atomic functions do not overlap, we can assume for $\varphi_{k,n}$ the expression

$$\varphi_{\vec{k},n}(r)=N^{-1/2}\textstyle\sum_{\nu} e^{i\vec{k}\cdot\vec{R}_{\nu}}\,U_{nlm}(\vec{r}-\vec{R}_{\nu})\,S(\sigma) \;, \qquad (2.21)$$

where $U_{nlm}$ is the $nlm$ orbital on the atom centered at $\vec{R}_{\nu}$. $S(\sigma)$ is the spin function. We may define the Fourier transform of a function $f(x,x')$ as

$$f(\vec{p},\vec{p}')=V^{-1}\int\int d^3x\,d^3x'\,e^{-i\vec{p}'\cdot\vec{x}}\,e^{i\vec{p}\cdot\vec{x}'}f(x,x') \quad . \qquad (2.22)$$

So we have for the Fourier transform of the exchange potential,

$$\langle\vec{p}'\,|\,V_{\rm ex}\,|\,\vec{p}\rangle=\frac{-e^2}{V}\int d^3r\,d^3r'$$

$$\times\sum_{\vec{k},n}\frac{\varphi_{\vec{k}n}(\vec{r})\,\varphi_{k,n}(\vec{r}')\,e^{i\vec{p}\cdot\vec{r}}\,e^{-i\vec{p}\cdot\vec{r}'}}{|\vec{r}-\vec{r}'|} \quad . \qquad (2.23)$$

In the Appendix we give an exact method, originally due to Brinkman, for calculating such matrix elements, the result being

$$\langle\vec{p}'\,|\,V_{\rm ex}\,|\,\vec{p}\rangle=\textstyle\sum_t P_t(\cos\theta)\,S_t(|\vec{p}|,\,|\vec{p}'|) \quad . \qquad (2.24)$$

Here $P_t$ are the Legendre polynomials,

$$\cos\theta=\vec{p}\cdot\vec{p}'/(|p|\,|p'|),\; S_t(|p|,\,|p'|)$$

are defined in the Appendix, where the convergence of the above series is also discussed.

Thus, everything is given. We can summarize this by saying that the problem now is to diagonalize the matrix

$$H^{\alpha}-ES^{\alpha} \quad , \qquad (2.25)$$

where $H^{\alpha}$ are the matrix elements

$$H^{\alpha,i}_{p,p'}=\delta_{p,p'}\,[\,|\vec{k}+\vec{K}_i|^2+V_c(0)]+\sum_{I\neq}\sum_{I'} b^{\alpha i *}_{pI}\,b^{\alpha i}_{p'I'}$$

$$\times\;V_c(|\vec{K}_I-\vec{K}_{I'}|)+\sum_{I}\sum_{I'} b^{\alpha i *}_{pI}\,b^{\alpha i}_{p'I'}\langle\vec{p}\,|\,V_{\rm ex}\,|\,\vec{p}'\rangle$$

$$-\sum_{nl} E_{nl} A_{nl}(p) A_{nl}(p')$$

$$\times \sum_{I} \sum_{I'} b_{pI}^{\alpha i *} b_{p'I'}^{\alpha i} P_l(\cos\theta_{II'}) \quad , \qquad (2.26)$$

and $S_\alpha$ is

$$S_{pp'}^{\alpha, i} = \delta_{pp'} - \sum_{nl} A_{nl}^{*}(|\vec{k}+\vec{K}_I|) A_{nl}(|\vec{k}+\vec{K}_{I'}|) \sum_{I} \sum_{I'}$$

$$\times\, b_{pI}^{\alpha i *} b_{p'I'}^{\alpha i} P_l(\cos\theta_{II'}) \quad , \qquad (2.27)$$

where all the quantities have been defined.

For the case in which the Slater approximation for the exchange is used, we can write $H$ as

$$H_{pp'}^{\alpha i} = \delta_{pp'} |\vec{k}+\vec{K}_I|^2 + \sum_{I} \sum_{I'} b_{pI}^{\alpha i *} b_{p'I'}^{\alpha i} V |\vec{K}_I - \vec{K}_{I'}|)$$

$$- \sum E_{nl} A_{nl}^{*}(p) A_{nl}(p') \sum_{I} \sum_{I'} b_{pI}^{\alpha i *} b_{p'I'}^{\alpha i} P_l(\cos\theta_{II'}) \quad , \qquad (2.28)$$

whereas $S$ is exactly the same. It is clear that the amount of work involved is large. Since the amount of work involved gets larger as we go from points of high symmetry to points of lower symmetry, we shall diagonalize the secular determinant only at points of high symmetry, i.e., $\Gamma$, $X$, $L$, $\Delta$, and $\Lambda$.

### B. Numerical Results for Argon

All the calculations have been performed using the CDC 6400 of Lehigh University and the CDC 6600 of the Computing Center of New York University. The computer language is FORTRAN IV.

#### 1. HF *Calculation*

We have used as atomic wave functions and energies the ones given by Watson and Freeman.[22] All the necessary quantities are shown in Table I. Since we have done all the integrations involved in the calculation numerically, except the one in the exchange potential, we have used, making some slight modifications, a program written by Fowler,[23] which transforms the Watson-Freeman wave functions from analytical to numerical form. In Table II, we show some values of $S_l(p, p')$ that appear in the expression for the exchange,

$$\langle \vec{p}' | V_{\text{ex}} | \vec{p} \rangle = \sum_l P_l(\cos\theta) S_l(p, p') \quad . \qquad (2.29)$$

Figure 1 shows the $p$ dependence of the exchange potential in the HF theory. This is important since this dependence disappears when the Slater approximation is made. The $A_{nl}$ are shown in Table III, and in Table IV we list some Fourier coefficients of the Coulomb part of the argon potential. We have calculated the band energies at $\Gamma$, including the 13 lowest values of $\vec{k}+\vec{K}_I$ at this point. At $X$, $L$, $\Delta$, and $\Lambda$ the calculation has been done including the

TABLE I. Atomic parameters for argon (Ref. 22). HF one-electron energies (in Ry). $E_{1s} = -237.212$, $E_{2s} = -24.638$, and $E_{2p} = 19.136$.

Eigenvectors $C_{ij}$ defined in Eq. (A10)

| $j$ | 1s | 2s | 3s | $j$ | 2p | 3p |
|---|---|---|---|---|---|---|
| 1 | 0.468439 | −0.124482 | 0.027819 | 10 | 0.024363 | −0.012406 |
| 2 | 0.519233 | −0.160026 | 0.066067 | 11 | 0.272699 | −0.042490 |
| 3 | 0.037833 | −0.149146 | 0.042169 | 12 | 0.745831 | −0.279285 |
| 4 | −0.049619 | 0.118307 | −0.048426 | 13 | −0.022530 | 0.156164 |
| 5 | 0.048353 | 0.733993 | −0.221211 | 14 | 0.029974 | 0.331960 |
| 6 | −0.019167 | 0.304248 | −0.213967 | 15 | −0.014849 | 0.574225 |
| 7 | 0.003608 | 0.025407 | 0.284222 | 16 | 0.002154 | 0.097973 |
| 8 | −0.002056 | −0.007514 | 0.714745 | | | |
| 9 | 0.000476 | 0.001891 | 0.151733 | | | |

Parameters $A_j$ and $Z_j$ defined in Eq. (A11)

| For $s$ orbitals ($l=0$) | | | For $p$ orbitals ($l=1$) | | |
|---|---|---|---|---|---|
| $j$ | $A_j$ | $Z_j$ | $j$ | $A_j$ | $Z_j$ |
| 1 | 0 | 20.0999 | 10 | 0 | 14.7820 |
| 2 | 0 | 15.6644 | 11 | 0 | 9.4975 |
| 3 | 1 | 15.6838 | 12 | 0 | 5.7870 |
| 4 | 1 | 10.3041 | 13 | 1 | 4.2264 |
| 5 | 1 | 7.2867 | 14 | 1 | 2.6757 |
| 6 | 2 | 6.8971 | 15 | 1 | 1.9232 |
| 7 | 2 | 3.7052 | 16 | 1 | 0.9649 |
| 8 | 2 | 2.5450 | | | |
| 9 | 2 | 1.5878 | | | |

TABLE II. Some values of $S_j(p,p')$ defined in Eq. (A28).

| $p$ | $p'$ | $S_0$ | $S_1$ | $S_2$ | $S_3$ | $S_4$ | $S_5$ | $S_6$ |
|---|---|---|---|---|---|---|---|---|
| 0 | 0 | −0.621 144 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 3 | 0 | −0.251 741 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 3 | 3 | −0.133 924 | −0.187 920 | −0.037 865 | −0.007 765 | −0.001 634 | −0.000 378 | −0.000 075 |
| 4 | 0 | −0.195 585 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 4 | 3 | −0.111 845 | −0.172 357 | −0.039 249 | −0.008 856 | −0.001 999 | −0.000 484 | −0.000 093 |
| 4 | 4 | −0.095 413 | −0.159 706 | −0.039 249 | −0.010 388 | −0.002 557 | −0.000 663 | −0.000 125 |
| 8 | 0 | −0.078 449 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 8 | 3 | −0.059 379 | −0.110 407 | −0.032 803 | −0.008 993 | −0.002 301 | −0.000 583 | −0.001 05 |
| 8 | 8 | −0.040 888 | −0.079 012 | −0.037 355 | −0.015 336 | −0.005 646 | −0.002 002 | −0.000 274 |
| 11 | 0 | −0.041 823 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 11 | 3 | −0.039 800 | −0.077 505 | −0.025 584 | −0.007 557 | −0.002 022 | −0.000 521 | −0.000 095 |
| 11 | 11 | −0.030 165 | −0.050 179 | −0.030 122 | −0.015 460 | −0.006 877 | −0.002 860 | −0.000 247 |
| 12 | 0 | −0.034 116 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 12 | 3 | −0.035 285 | −0.068 937 | −0.023 372 | −0.017 035 | −0.001 904 | −0.000 492 | −0.000 090 |
| 12 | 12 | −0.028 137 | −0.044 006 | −0.027 872 | −0.015 181 | −0.007 110 | −0.003 091 | −0.000 201 |
| 16 | 3 | −0.023 207 | −0.043 509 | −0.016 023 | −0.005 114 | −0.001 431 | −0.000 374 | −0.000 071 |
| 16 | 16 | −0.022 945 | −0.028 763 | −0.020 414 | −0.013 441 | −0.007 440 | −0.003 742 | −0.000 160 |
| 24 | 24 | −0.017 188 | −0.017 998 | −0.011 689 | −0.009 659 | −0.006 687 | −0.004 105 | 0.001 511 |

lowest 22 values of $\vec{k}+\vec{K}_I$.

In order to test the convergence of the valence and conduction energies as a function of the number of plane waves involved in the secular determinant, we have repeated the calculation at Γ using more sets of plane waves. Figure 2 represents the convergence test. The energy bands so obtained are shown in Fig. 3.

It is observed that generally the convergence is excellent, except for the uppermost $3p$ band. This is something common and has been seen before by other people. Reilly[10] had the same results in his calculation for xenon, and Kunz[11] has seen the same effect in his numerous calculations for alkali halides. Reilly has proposed two possible explanations. The first possibility involves the fact that for a $p$ function the cancellation between $V$ and the repulsive pseudopotential $V_R$ coming from orthogonalization to core states is not complete because $V_R$ takes into account only the kinetic term of the radial motion and does not include the angular kinetic term $l(l+1)/r^2$. A second possibility is that, since the valence wave functions are tightly bound to the nuclei and are not spread over a large extent, a large number of OPW are required in order to describe the rapid oscillations in regions where the kinetic energy is more important. In effect, a very good explanation for the poor convergence of the $p$ valence bands has been given by Deegan and Twose.[24] The fact that the state $(3s)$ is so well

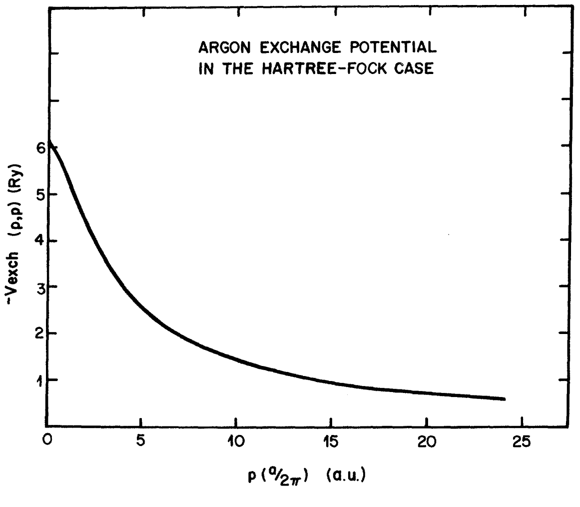

FIG. 1. Momentum dependence of the HF exchange.

TABLE III. Orthogonalization coefficients for argon at the Γ point. HF case [see Eq. (1.14)].

| $K^2$ | $(1s)$ | $(2s)$ | $(2p)$ |
|---|---|---|---|
| 0 | 0.012 26 | 0.096 51 | 0.000 00 |
| 3 | 0.012 04 | 0.086 50 | 0.034 39 |
| 4 | 0.012 02 | 0.083 69 | 0.038 74 |
| 8 | 0.011 92 | 0.073 61 | 0.048 61 |
| 11 | 0.011 82 | 0.067 05 | 0.051 96 |
| 12 | 0.011 79 | 0.065 03 | 0.052 67 |
| 16 | 0.011 65 | 0.057 68 | 0.054 23 |
| 19 | 0.011 56 | 0.052 83 | 0.054 51 |
| 20 | 0.011 52 | 0.051 33 | 0.054 48 |
| 24 | 0.011 40 | 0.045 82 | 0.053 96 |
| 27 | 0.011 31 | 0.042 16 | 0.053 25 |
| 32 | 0.011 17 | 0.036 78 | 0.051 67 |
| 35 | 0.011 08 | 0.033 94 | 0.050 58 |
| 36 | 0.011 06 | 0.033 05 | 0.050 20 |
| 40 | 0.010 95 | 0.029 74 | 0.048 62 |
| 43 | 0.010 86 | 0.027 50 | 0.047 41 |
| 44 | 0.010 84 | 0.026 80 | 0.047 00 |

TABLE IV. Fourier coefficients for the argon Coulomb potential (Ry). HF case.

| $K^2$ | $V_C(K)$ | $K^2$ | $V_C(K)$ |
|---|---|---|---|
| 0 | −0.407 941 | 21 | −0.114 721 |
| 1 | −0.365 624 | 22 | −0.110 709 |
| 2 | −0.331 893 | 24 | −0.103 470 |
| 3 | −0.303 924 | 27 | −0.094 239 |
| 4 | −0.280 173 | 32 | −0.082 116 |
| 5 | −0.259 679 | 35 | −0.076 293 |
| 6 | −0.241 788 | 36 | −0.074 542 |
| 8 | −0.212 051 | 40 | −0.068 331 |
| 9 | −0.199 571 | 43 | −0.064 366 |
| 10 | −0.188 371 | 44 | −0.063 154 |
| 11 | −0.178 272 | 48 | −0.058 788 |
| 12 | −0.169 128 | 51 | −0.055 917 |
| 13 | −0.160 817 | 56 | −0.051 790 |
| 14 | −0.153 236 | 59 | −0.049 630 |
| 16 | −0.139 932 | 64 | −0.046 455 |
| 17 | −0.134 073 | 68 | −0.044 233 |
| 18 | −0.128 666 | 72 | −0.042 243 |
| 19 | −0.123 665 | 76 | −0.040 449 |
| 20 | −0.119 129 | | |

converged indicates that our core states are very good eigenstates of our crystal Hamiltonian. We also note that the 3*s* and 3*p* valence bands lie approximately at the same position as the atomic 3*s* and 3*p* states, as shown in Fig. 2.

The most interesting characteristic, however, is the relatively large gap, about 17 eV, between the top of the valence band and the bottom of the conduction band. Experimentally, the gap, as deducted from optical measurements by Baldini, should be about 14.3 eV. This characteristic will be discussed later.

Another characteristic of the above results is the fact that the valence bands have a relatively large width. This is also in agreement with other HF calculations. Howland[25] also found, in his calculation for KCl, relatively wide valence bands; calculations by Kunz[26] for alkali halides also confirm the above result. Incidentally, we note that the agreement between our calculation and the one by Mattheiss using the augmented-plane-wave (APW) method is only qualitative in the sense that the order of the energy levels is the same in both cases but the separations are different. We will later discuss more extensively the HF results.

### 2. *Hartree-Fock-Slater Calculation*

We have previously noted that it is extremely important to use, in the OPW method, core states that are exact eigenstates of the crystal Hamiltonian. When the Slater approximation for the exchange is made, we cannot use the same energies and wave functions as in the preceding calculation. We have, therefore, calculated the core energies

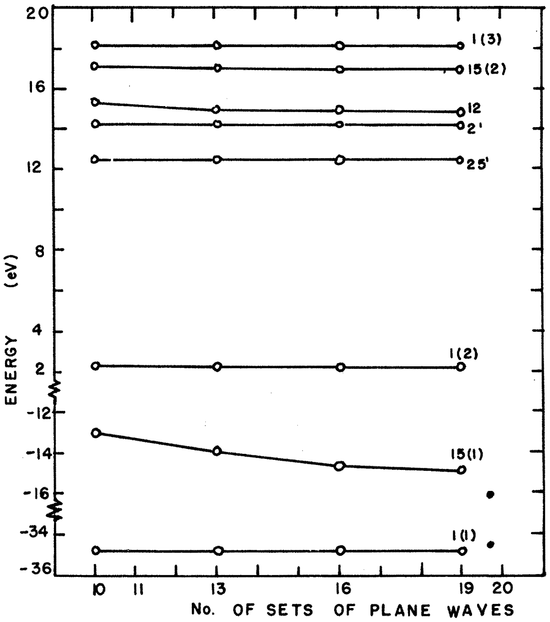

FIG. 2. Convergence test at Γ. Plotted are the energies calculated for the various irreducible representations at Γ versus the number of sets of plane waves used.

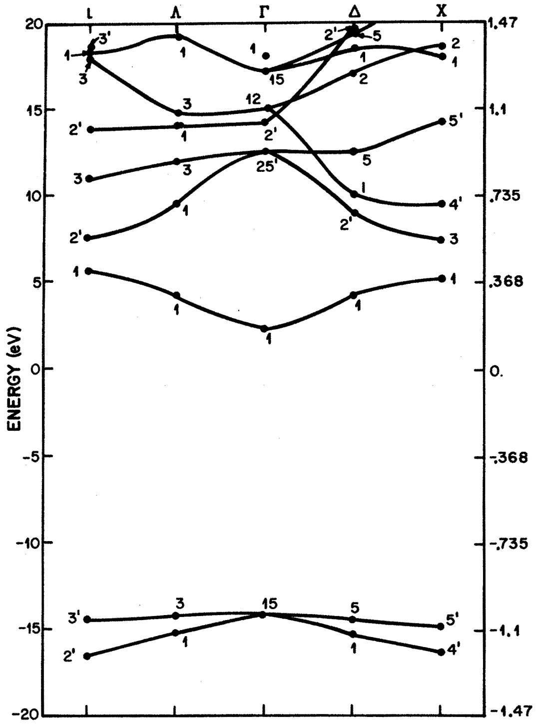

FIG. 3. Argon energy bands in the HF case. The numbers on the figure refer to the irreducible representations corresponding to particular *k* values.

TABLE V. Atomic energies for argon. Comparison between solutions using the Slater approximation for the exchange and a modified Slater exchange.

| | Energies (Ry) | | | |
|---|---|---|---|---|
| State | Slater | Slater corrected | | |
| 1*s* | − 232.448 23 | − 232.5358 | − 232.54 | (Ref. 27) |
| 2*s* | − 22.785 4 | − 22.8649 | − 22.865 | (Ref. 27) |
| 3*s* | − 2.052 6 | − 2.1069 | − 2.1068 | (Ref. 27) |
| 2*p* | − 18.127 2 | − 18.2077 | − 18.2075 | (Ref. 27) |
| 3*p* | − 1.006 9 | − 1.0655 | − 1.0653 | (Ref. 27) |

using a program written by Herman and Skillman.[27] In Table V, we show the atomic energies for argon using the Slater approximation and we compare them with the energies obtained with the use of the corrected approximation, i.e., when we write the atomic potential as

$$V(r)=-\frac{2Z}{r}-\frac{2}{r}\int_0^r \sigma(r')\,dr'-2\int_r^\infty \frac{\sigma(r')}{r'}\,dr'$$

$$-6\left(\frac{3}{8\pi}\frac{\sigma(r)}{4\pi r^2}\right)^{1/3}, \quad r\leq R_0 \tag{2.30}$$

$$V(r)=-2(Z-N+1)/r, \quad r>R_0\ . \tag{2.31}$$

where $R_0$ is defined as that radius at which the value of $V(r)$ given by Eq. (2.30) equals the value of $V(r)$ given by Eq. (2.31). Table VI shows the orthogonalization coefficients. The Fourier transforms of the total potential are shown in Table VII. An energy-band calculation has been done using the 10 lowest sets of plane waves at Γ and the lowest 16 at *X*, *L*, Δ, and Λ. Results are plotted in Fig. 4.

The main difference between these bands and those we have obtained previously is a change in the energy gap. In this case, the gap is about 7 eV. The inclusion of more plane waves could make the gap about 8 eV. This time, therefore, the calculated gap is considerably smaller than the experimental one. Other differences are the change of the position of some bands. This change is small compared to the change in the value of the energy gap, and it looks as if the difference in the two calculations is mainly a shift of the conduction bands. The large width of the valence bands is perhaps due to the small gap. It is important to note that the gap obtained by this calculation is very different than the one obtained by Mattheiss.[7] This is because, even if Mattheiss also used the Slater approximation for the exchange potentials, he made the "muffin-tin" approximation and used the crystal change density $\rho$ to the one-third; whereas we have treated our crystal Slater exchange as a simple sum of atomic Slater exchanges, which is, in effect, a very poor way of treating the exchange potential.

TABLE VI. Orthogonalization coefficients for argon at the Γ point. Hartree-Fock-Slater case [Eq. (2.14)].

| $K^2$ | (1*s*) | (2*s*) | (2*p*) |
|---|---|---|---|
| 0 | 0.012 05 | 0.095 31 | 0.000 00 |
| 3 | 0.011 95 | 0.086 28 | 0.033 86 |
| 4 | 0.011 92 | 0.083 51 | 0.037 86 |
| 8 | 0.011 80 | 0.073 52 | 0.047 32 |
| 11 | 0.011 71 | 0.067 00 | 0.050 82 |
| 12 | 0.011 68 | 0.064 99 | 0.051 58 |
| 16 | 0.011 56 | 0.057 66 | 0.053 34 |
| 19 | 0.011 47 | 0.052 82 | 0.053 70 |
| 20 | 0.011 44 | 0.051 32 | 0.053 70 |
| 24 | 0.011 33 | 0.045 80 | 0.053 22 |
| 27 | 0.011 24 | 0.042 13 | 0.052 53 |
| 32 | 0.011 10 | 0.036 75 | 0.050 97 |
| 35 | 0.011 02 | 0.033 91 | 0.049 89 |
| 36 | 0.010 99 | 0.033 02 | 0.049 51 |
| 40 | 0.010 89 | 0.029 72 | 0.047 96 |
| 43 | 0.010 81 | 0.027 48 | 0.046 77 |
| 44 | 0.010 78 | 0.026 78 | 0.046 37 |

## III. ENERGY BANDS WITH CORRELATION

### A. General Remarks

The calculations that we have performed so far have been in the limit of the HF approximation. As already mentioned, no correlation is included in the approximation except for that coming from the assumption of a totally antisymmetric electronic wave function. The problem of including correlation effects in an energy-band calculation has been discussed by many people. There are essentially two different ways of including these

TABLE VII. Fourier coefficients for the argon potential $V_C + V_{\text{ex. Slater}} = V(r)$ (in Ry).

| $K^2$ | $V(K)$ | $K^2$ | $V(K)$ |
|---|---|---|---|
| 0 | −1.298 949 | 21 | −0.117 484 |
| 1 | −0.722 256 | 22 | −0.113 630 |
| 2 | −0.522 223 | 24 | −0.110 040 |
| 3 | −0.420 141 | 27 | −0.100 602 |
| 4 | −0.357 300 | 32 | −0.088 250 |
| 5 | −0.313 839 | 35 | −0.082 306 |
| 6 | −0.281 534 | 36 | −0.080 515 |
| 8 | −0.235 892 | 40 | −0.074 138 |
| 9 | −0.218 883 | 43 | −0.070 041 |
| 10 | −0.204 444 | 44 | −0.068 784 |
| 11 | −0.191 989 | 48 | −0.064 218 |
| 12 | −0.181 110 | 51 | −0.061 210 |
| 13 | −0.171 497 | 56 | −0.058 815 |
| 14 | −0.162 929 | 59 | −0.054 508 |
| 16 | −0.148 299 | 64 | −0.051 072 |
| 17 | −0.141 997 | 68 | −0.048 641 |
| 18 | −0.136 245 | 72 | −0.046 445 |
| 19 | −0.130 961 | 76 | −0.044 449 |
| 20 | −0.126 116 | | |

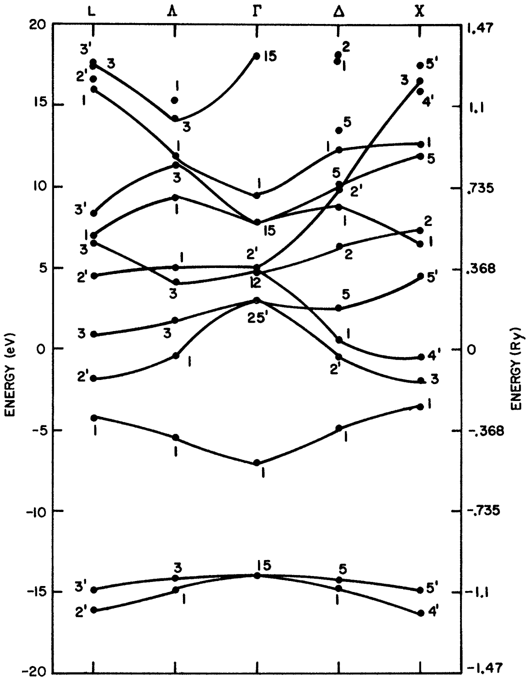

FIG. 4. Argon energy bands obtained using the Slater approximation for the exchange potential. The numbers on the figure have the same meaning as in Fig. 3.

effects, one which we will call an excitoniclike approach and the other which we will call a quasiparticle one. The former shows that electronic polarization effects can be accounted for by shifting in an appropriate way the position of the valence and conduction bands calculated in the HF approximation. The latter allows correlation to be incorporated into the band Hamiltonian through an effective one-electron potential. In what follows, we will describe first the quasiparticle approach, following quite heavily the notation of Brinkman.[28] After that, we will outline the other approach in order to compare the two.

### B. Exact Equations for Electron System

Following Brinkman,[28] it is possible to write a one-particle equation which includes dielectric effects as

$$[\epsilon_i - h(x) - V(x)] f_i(x) - \int M(x, x', \epsilon_i) f_i(x')\,dx' = 0 \quad , \tag{3.1}$$

where

$$h(x) = \left( \frac{-\nabla^2}{2m} - \sum_\nu \frac{Ze^2}{|\vec{r} - \vec{R}_\nu|} \right) \quad ,$$

and $V(x)$ is the Coulomb potential. This is an effective one-particle equation and all the correlation is included in the self-energy operator $M$.

When the states $f_i$ are supposed to be one-particle functions of single Slater determinants, then $M$ reduces to the HF exchange. The HF equations are, therefore, a particular case of the more general effective one-electron wave equations. For a given eigenvalue $\epsilon_i$, the operator

$$h_{\text{eff}} = h(x) + V(x) + M(x, x', \epsilon_i)$$

has an eigenvalue spectrum $\bar{\epsilon}_t(\epsilon_i)$ and a corresponding set of eigenfunctions $\bar{f}_t$. If we denote with $\bar{f}_{nc}$ the wave functions for the core states, we can define again the projection operator

$$\bar{P}_c = \sum_{nc} |\bar{f}_{nc}\rangle \langle \bar{f}_{nc}| \quad . \tag{3.2}$$

It is to be noted, however, that $h_{\text{eff}}$ is not necessarily Hermitian, and, therefore, the $\bar{f}_{nc}$ need not be orthogonal; however, we may expect that the nonhermiticity is small for core-type solutions so that we can still apply the OPW method for the determination of the valence and conduction bands by writing for these states

$$f_i = (1 - \bar{P}_c)\,\varphi_i(x) \quad . \tag{3.3}$$

Substitution into Eq. (3.1) gives

$$[\epsilon_s - h(x) - V(x)]\,\varphi_s(x) - \int d^3x\, M(x, x', \epsilon_s)\,\varphi_s(x') + \sum_{nc} (\epsilon_s - \bar{\epsilon}_{nc}) \bar{P}_{nc}\,\varphi_s(x) = 0 \quad . \tag{3.4}$$

This is an exact formulation of the generalized OPW equations in which the correlation has been included. An exact self-consistent calculation of these equations is not possible. However, Eq. (3.4) certainly represents a convenient starting point for approximations which go beyond the HF approximation. In what follows, we will consider only the first term in $M$. This corresponds to the random-phase approximation for the self-energy operator.

So we write

$$M(x, x', \epsilon) = i \int d(t - t')\, e^{i\epsilon(t-t')}\, W(x, x')\, G(x, x') \quad , \tag{3.5}$$

where $W(x, x')$ is the screened interaction potential, and $G(x, x')$ is the Green's function.[28] The total contribution to $G$ and $W$ can be divided in two parts, core electron excitations and valence electron excitations. Therefore, $G$ and $W$ can be rewritten as

$$G(x, x', \epsilon) = G_c(x, x', \epsilon) + G_v(x, x', \epsilon) \quad , \tag{3.6}$$

$$W(x, x', \epsilon) = W_c + W_v \quad , \tag{3.7}$$

where

$$G_c = \sum_{nc} \frac{f^*_{nc}(x)\, f_{nc}(x')}{\epsilon - \epsilon_{nc}} \quad , \tag{3.8}$$

and similar expressions for $M_v$ and $W_v$. Thus, we can write

$$M=(W_c+W_v)G_c+(W_c+W_v)G_v\ . \qquad (3.9)$$

It can be shown[28] that the first two terms can be reduced to the unscreened core exchange potential for the following two reasons: (i) The core energies are large compared to the plasma valence energies ($\omega_p^2=4\pi Ne^2/m$; for argon $\omega_p=16.6$ eV) and (ii) core excitations are spread over a large range of momentum and energy. The third term

$$W_cG_v \qquad (3.10)$$

represents the core polarization term and we will neglect it in our calculation.

All the correlation and exchange between valence electrons is therefore, included in the term $W_vG_v$. Therefore, we can write

$$\begin{aligned} M(x,x',\epsilon)&=V_{\rm ex}^c(x,x')+M_v(x,x',\epsilon)\\ &=V_{\rm ex}^c(x,x')+i\int_{\infty}^{\infty}\frac{d\epsilon'}{(2\pi)}\,e^{-i\epsilon'\Delta}\,W_v(x,x',\epsilon)\\ &\quad\times G(x,x',\epsilon-\epsilon')\ . \end{aligned} \qquad (3.11)$$

Here,

$$V_{\rm ex}^c(x,x')=\sum_{nc}\frac{f_{nc}^*(x)\,f_{nc}(x')}{|\vec{r}-\vec{r}'|}\ . \qquad (3.12)$$

We now write the effective interaction $W$ in terms of the dynamic dielectric function $\epsilon(x'',x',\epsilon)$ as

$$W(x,x',\epsilon)=\int v(x-x'')\,\epsilon^{-1}(x'',x',\epsilon)\,d^3x''\ . \qquad (3.13)$$

If we now write

$$\begin{aligned} W(\epsilon)e^{-i\epsilon\Delta}&=[v(q)/\epsilon(\epsilon)]e^{-i\epsilon\Delta}=v(q)e^{-i\epsilon\Delta}\\ &\quad+v(q)\{[\epsilon(q,0)]^{-1}-1\}\\ &\quad+v(q)\,[\epsilon(q,\epsilon)-\epsilon(q,0)]^{-1}\ , \end{aligned} \qquad (3.14)$$

and we neglect the last term, we obtain an expression for the effective interaction which is independent of the energy. In this case, we can perform the integral in (3.11) by enclosing the contour at infinity. Thus we get

$$\begin{aligned} M_v&=-\int d^3x''v(x-x'')\,\epsilon^{-1}(x'',x',0)\,\rho_v(x,x')\\ &\quad+\tfrac{1}{2}\int dx''v(x-x'')\,[\epsilon^{-1}(x'',x',0)-\delta(x''-x')]\\ &\quad\times[\delta(x-x')-\langle x|\overline{P}_c|x\rangle]\ . \end{aligned} \qquad (3.15)$$

Here we have used the relationship

$$\begin{aligned} \sum_s f_s(x)\,f_s^*(x'')=\delta^3(x-x')&=\sum_{nv}f_{nv}(x)\,f_{nv}^*(x')\\ &\quad+\sum_{nc}f_{nc}(x)\,f_{nc}^*(x')\ . \end{aligned} \qquad (3.16)$$

The first term in Eq. (3.15) is the static screened valence exchange; the second is the static Coulomb-hole self-potential for a particle which is not in a core state.

Taking the Fourier transform according to

$$M(\vec{p},\vec{p}')=\int\int d^3x\,d^3x'\,e^{i\vec{p}\cdot\vec{x}'}M(x,x')\,e^{-i\vec{p}'\cdot\vec{x}}\ , \qquad (3.17)$$

we get for the first term in (3.4) that we call $V_{sx}$,

$$\begin{aligned} V_{sx}(\vec{p},\vec{p}+\vec{K})&=-\int dx\int dx'\,e^{i\vec{p}\cdot\vec{x}'}e^{-i(\vec{p}+\vec{K})\cdot\vec{x}}\\ &\quad\times v(x-x'')\,\epsilon^{-1}(x'',x',0)\\ &\quad\times\sum_{nv,\,\epsilon_{nv}<\mu}f_{nv}(x)\,f_{nv}^*(x')\ . \end{aligned} \qquad (3.18)$$

Here, $\mu$ is the chemical potential. Now, for the case of a solid with a periodic lattice we can write

$$\begin{aligned} \epsilon^{-1}(x'',x',0)&=\int\frac{d^3q}{(2\pi)^3}\sum_I e^{-i\vec{K}_I\cdot\vec{x}''}\\ &\quad\times\epsilon^{-1}(\vec{q},\vec{q}+\vec{K}_I,0)\,e^{i(\vec{q}+\vec{K}_I)\cdot x'}\ . \end{aligned} \qquad (3.19)$$

Thus we get

$$\begin{aligned} V_{sx}(\vec{p},\vec{p}+\vec{K})&=-\int\frac{d^3\vec{q}}{(2\pi)^3}\,v(q)\sum_{\vec{G}}\epsilon^{-1}(\vec{q},\vec{q}+\vec{G},0)\\ &\quad\times\sum_{nv,\,\epsilon_{nv}<\mu}f_{nv}(\vec{p}-\vec{q})\,f_{nv}^*(\vec{p}-\vec{q}-\vec{G})\ , \end{aligned} \qquad (3.20)$$

where $\vec{K}$ and $\vec{G}$ are reciprocal-lattice vectors. The terms $\vec{G}\neq 0$ in (3.20) (nondiagonal terms) represent the local-field effects. Since it is extremely hard to calculate them and also since they are small in most cases, we will neglect them. Therefore, we may write

$$\begin{aligned} M_v(\vec{p},\vec{p}+\vec{K})&=-\int\frac{d^3\vec{q}}{(2\pi)^3}\,\frac{v(q)}{\epsilon(q)}\sum_{nv,\,\epsilon_{nv}<\mu}f_{nv}(\vec{p}-\vec{q})\\ &\quad\times f_{nv}(\vec{p}+\vec{K}-\vec{q})+\frac{1}{2}\int\frac{d^3q}{(2\pi)^3}\,v(q)\left(\frac{1}{\epsilon(q,0)}-1\right)\\ &\quad\times(\delta_{\vec{K},0}-\langle\vec{p}-\vec{q}|\overline{P}_c|\vec{p}+\vec{K}-\vec{q}\rangle)\ . \end{aligned} \qquad (3.21)$$

If we now assume, as a final simplification, that the matrix elements of $P_c$ do not vary very rapidly in the region of integration, this region being determined by the fact that $\epsilon(q)\sim 1$ for $q\sim 2\pi/a$, we can finally write

$$\begin{aligned} M(\vec{p},\vec{p}+\vec{K})&=V_{\rm ex}^c(\vec{p},\vec{p}+\vec{K})+V_v^{\rm SCH}(\vec{p},\vec{p}+\vec{K})\\ &\quad+E_{\rm CH}(\delta_{0,\vec{K}}-\langle\vec{p}|\overline{P}_c|\vec{p}+\vec{K}\rangle)\ , \end{aligned} \qquad (3.22)$$

where

$$\begin{aligned} V_{\rm ex}^c(\vec{p},\vec{p}+\vec{K})&=-\sum_{nc}\int\frac{d^3\vec{q}}{(2\pi)^3}\,v(q)\,f_{nc}(\vec{p}-\vec{q})\\ &\quad\times f_{nc}^*(\vec{p}-\vec{q}+\vec{K})\ , \end{aligned} \qquad (3.23a)$$

$$V_v^{\rm SCH}(\vec{p},\vec{p}+\vec{K})=-\sum_{nv,\,\epsilon_{nv}<\mu}\int\frac{d^3q}{(2\pi)^3}\,\frac{v(q)}{\epsilon(q)}\,f_{nv}(\vec{p}-\vec{q})$$

$$\times \; f^*_{nv}(\vec{p}-\vec{q}+\vec{K}) \; , \tag{3.23b}$$

$$E_{\mathrm{CH}}=\frac{1}{2}\int \frac{d^3q}{(2\pi)^3}\, v(q)\left(\frac{1}{\epsilon(q)}-1\right) . \tag{3.23c}$$

It is important to note that, in the above form, the Coulomb hole seen by the valence electrons is not seen by the core electrons since it occurs at $E_{\mathrm{CH}}(1-\overline{P}_c)$. This fact, along with the fact that the screened exchange acts only on the valence electrons, shows that the total operator $M$ becomes equal to the core exchange operator plus a small term when acting on a core function. Also, in this approximation, the Coulomb hole does not contribute to the shape of the valence bands. This would not be true if nondiagonal terms of the dielectric function were included.

Proceeding in a way analogous to the case of the HF equations, it is easy to show that to solve the Eq. (3.4) is the same as to diagonalize the determinant

$$H^\alpha - ES^\alpha , \tag{3.24}$$

where $H$ now has as matrix elements,

$$\begin{aligned} H^{\alpha,i}_{p,p'} &= \delta_{p,p'}\left[\,|k+K_I|^2+v_c(0)\right]+\sum_{I\neq I'}\sum b^{\alpha i}_{pI}{}^* b^{\alpha i}_{p'I'} \\ &\times v_c(|\vec{K}_I-\vec{K}_{I'}|)+\delta_{pp'}E_{\mathrm{CH}}+\sum_{I}\sum_{I'} b^{\alpha i}_{pI}{}^* b^{\alpha i}_{p'I'} \\ &\times \left[V^c_{\mathrm{ex}}(p,p')+V^{\mathrm{SCH}}_v(p,p')\right]-\sum_{nl}\sum_{I}\sum_{I'}(E_{\mathrm{CH}}+\overline{\epsilon}_{nl}) \\ &\times b^{\alpha i}_{pI}{}^* b^{\alpha i}_{p'I'} A^*_{nl}(p)A_{nl}(p')P_l(\cos\theta_{II'}) , \end{aligned} \tag{3.25}$$

and $S$ is the same as before, i.e.,

$$\begin{aligned} S^{\alpha,i}_{p,p'} &= \delta_{p,p'}-\sum_{nl}A_{nl}(p)A_{nl}(p')\sum_{I}\sum_{I'} b^{\alpha i}_{pI}{}^* b^{\alpha i}_{p'I'} \\ &\times P_l(\cos\theta_{II'}) . \end{aligned} \tag{3.26}$$

Here, $\overline{\epsilon}_{nl}$ are the core energies consistent with the new Hamiltonian. These energies are *a priori* different than those obtained from a solution of the HF equations. However, since the Coulomb hole does not act on a core electron and since the screening does not involve the core states, we can suppose that the difference between $\overline{\epsilon}_{nl}$ and $\epsilon_{nl}$ is small enough that we can neglect it.

As we can see, the above matrix elements require the knowledge of the dielectric function. This function has been calculated[29] using a model originally proposed by Fry.[30] This is discussed more fully elsewhere.[29]

## IV. NUMERICAL RESULTS FOR ARGON

Since the exact expression for the dielectric function is too complicated, we will use an interpolation formula in order to make the calculations more feasible. The interpolation formula will be

$$\epsilon(q)=1+\left[A/(1+Bq^2)^2\right] , \tag{4.1}$$

where the parameters $A$ and $B$ are calculated by fitting our numerical results. The self-energy integral $E_{\mathrm{CH}}$ can then be calculated exactly, giving

$$\begin{aligned} E_{\mathrm{CH}} &= \tfrac{1}{2}\int\left[d^3\vec{q}/(2\pi)^3\right] v(\vec{q})\left[1/\epsilon(q)-1\right] \\ &= -(A/cq^3)\cos\tfrac{1}{2}\alpha/\sin\alpha , \end{aligned} \tag{4.2}$$

where

$$q=(a/c)^{1/4}; \quad \cos\alpha=-b/(2(ac)^{1/2}) ,$$

$$a=1+A, \quad b=2B, \quad c=B^2 . \tag{4.3}$$

In order to see how sensitive this integral is with respect to the choice of the dielectric function, we have calculated the self-energy integral for different dielectric functions. Results are shown in Table VIII.

According to the argument presented earlier, the core functions are very weakly changed when correlation is taken into account; therefore, the core energies calculated in the HF approximation should be very close to the ones one would obtain if correlation is taken into account. We will then assume that the HF core energies are good also in this case.

The expression for the screened exchange matrix elements will be exactly the same as in the case of HF, i.e., we can still write

$$\langle\vec{p}\,|V^{\mathrm{scr}}_{\mathrm{exch}}|\,\vec{p}\,'\rangle=\sum_{l=0}^{\infty}P_l(\cos\theta)S^{\mathrm{corr}}_l(p,p') . \tag{4.4}$$

The difference in this case will be that the expression $S^{\mathrm{corr}}_l(p,p')$ will be

$$S^{\mathrm{corr}}_l(p,p')=S^{\mathrm{core}}_l+S^{\mathrm{val}}_l , \tag{4.5}$$

where $S^{\mathrm{core}}_l$ are the same as the corresponding HF results, and $S^{\mathrm{val}}_l$ is similar in the sense that it looks the same but contains the screening. Table IX shows the matrix elements for some values of $p$ and $p'$. In Fig. 5, we plot $\langle\vec{p}\,|V^{\mathrm{scr}}_{\mathrm{exch}}|\,\vec{p}\,\rangle$ versus $p$. As we may see, the $p$ dependence of the elements is not as strong as in the case of HF. As the screening increases, this dependence becomes

TABLE VIII. Self-energy integrals using different dielectric functions.

|  | $E_{CH}$ (Ry) |
|---|---|
| Hermanson dielectric function | −0.2856 |
| Penn dielectric function | −0.2750 |
| Our dielectric function | −0.1759 |
| Haken-Schottky-Fowler dielectric function | −0.0813 |

TABLE IX. Some values of $S_j^{\text{corr}}$ $(p,p')$, defined in Eq. (4.5).

| $p$ | $p'$ | $S_0^{\text{corr}}$ | $S_1^{\text{corr}}$ | $S_2^{\text{corr}}$ | $S_3^{\text{corr}}$ | $S_4^{\text{corr}}$ | $S_5^{\text{corr}}$ | $S_6^{\text{corr}}$ |
|---|---|---|---|---|---|---|---|---|
| 0 | 0 | −0.497 501 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 3 | 0 | −0.212 798 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 3 | 3 | −0.119 567 | −0.149 547 | −0.033 786 | −0.007 175 | −0.001 529 | −0.000 355 | −0.000 070 |
| 4 | 0 | −0.167 660 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 4 | 3 | −0.101 236 | −0.138 696 | −0.035 349 | −0.008 253 0 | −0.001 886 7 | −0.000 459 | −0.000 088 |
| 4 | 4 | −0.087 517 | −0.130 096 | −0.037 634 | −0.009 757 | −0.002 432 | −0.000 634 | −0.000 119 |
| 8 | 0 | −0.071 659 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 8 | 3 | −0.056 439 | −0.091 364 | −0.030 139 | −0.008 227 9 | −0.002 209 | −0.000 565 | −0.000 102 |
| 8 | 8 | −0.040 153 | −0.069 171 | −0.035 374 | −0.014 857 | −0.005 517 | −0.001 964 | −0.000 268 |
| 11 | 0 | −0.040 902 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 11 | 3 | −0.039 168 | −0.064 984 | −0.023 687 | −0.007 212 | −0.001 953 | −0.000 506 | −0.000 093 |
| 11 | 11 | −0.030 067 | −0.045 759 | −0.028 996 | −0.015 130 | −0.006 775 | −0.002 826 | −0.000 243 |
| 12 | 0 | −0.034 349 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 12 | 3 | −0.035 126 | −0.058 017 | −0.021 679 | −0.006 725 | −0.001 842 | −0.000 479 | −0.000 088 |
| 12 | 12 | −0.028 083 | −0.040 597 | −0.026 940 | −0.014 896 | −0.007 017 | −0.003 058 | −0.000 197 |
| 16 | 3 | −0.024 145 | −0.037 132 | −0.014 939 | −0.004 911 | −0.001 391 | −0.000 366 | −0.000 069 |
| 16 | 16 | −0.022 872 | −0.027 530 | −0.019 966 | −0.013 278 | −0.007 377 | −0.003 716 | −0.000 771 |
| 24 | 24 | −0.017 0134 | −0.017 842 | −0.011 574 | −0.009 603 | −0.006 659 | −0.004 091 | 0.001 510 |

weaker and weaker. This is perhaps a reason why the Slater approximation works well in the case of semiconductors, since the Slater approximation does not show any $p$ dependence.

We now have all the ingredients necessary for the band calculation. We have calculated the energies at the points $\Gamma$, $X$, $L$, $\Delta$, and $\Lambda$. Figure 6 shows the corresponding energy bands. The above calculation includes 13 sets of plane waves at $\Gamma$ and 22 at $X$, $L$, $\Delta$, and $\Lambda$. In order to check the convergence, we have recalculated the energy levels at $\Gamma$ including ten and more sets of plane waves. Table X shows the results at $\Gamma$.

An extensive discussion of the results will be given in Sec. V. However, at this point it is noteworthy that we have computed an energy gap of 13.7 eV, which is to be compared with the experimental value 14.3 eV obtained by Baldini.[31] The agreement is very good. Incidentally, we also note that the value for the gap obtained by Mattheiss[7] is 13.3

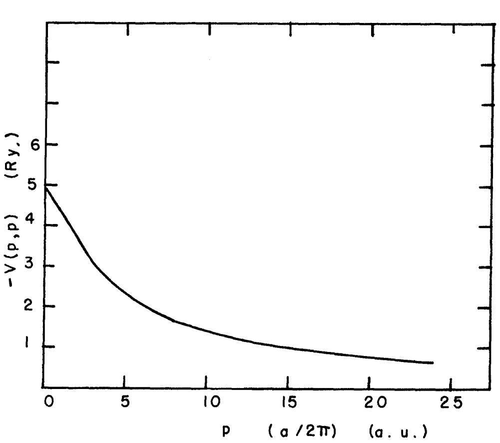

FIG. 5. Momentum dependence of the exchange potential with valence screening.

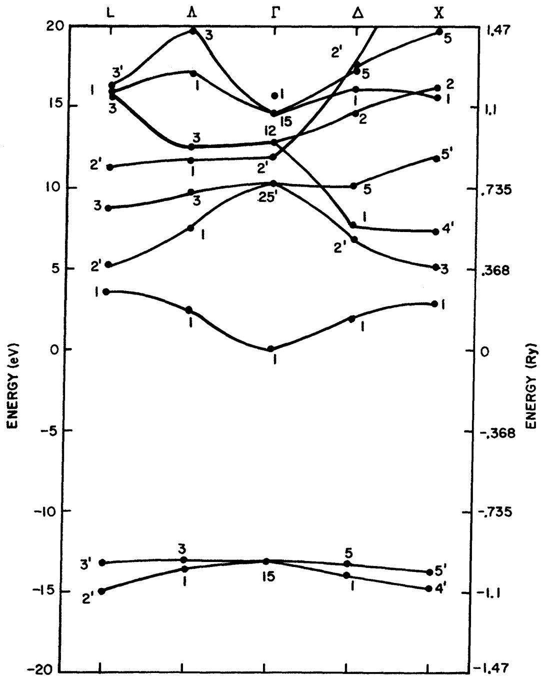

FIG. 6. Argon energy bands with correlation effects included. The numbers in the figure have the same meaning as in Figs. 3 and 4.

TABLE X. Energies calculated for different numbers of sets of plane waves at Γ. Calculation with correlation.

| Irreducible representations | Energies (in eV)<br>Plane wave up to ⟨422⟩ | Plane wave up to ⟨440⟩ | Plane waves up to ⟨622⟩ |
|---|---|---|---|
| $\Gamma_1$ | −32.6710 | −32.6811 | −32.6890 |
| | 0.0645 | 0.0601 | 0.0577 |
| | 15.8082 | 15.8071 | 15.8060 |
| $\Gamma_{15}$ | −11.8672 | −12.7562 | −13.6371 |
| | 14.8255 | 14.7753 | 14.7241 |
| $\Gamma_{25}'$ | 10.3326 | 10.3296 | 10.3217 |
| $\Gamma_{12}$ | 13.2086 | 12.9954 | 12.8747 |
| $\Gamma_2'$ | 11.9361 | 11.9302 | 11.9296 |

eV, and the one obtained by Knox and Bassani[6] is 12.4 eV. We also observe that the width of the $p$ valence bands is still large but smaller than that obtained in the HF approximation calculation. Comparing this last calculation, including correlation, with the HF one we see that the main difference in the two is a change of the energy gap, while we have a small difference in the shape; in particular, the valence bands go up and the conduction bands go down. This is in agreement with Fowler's calculation of the effect of electronic correlation, which we will outline in order to have a better understanding of the above characteristic.

### A. Electronic Correlation in Excitonic Theory

Following the theory of Haken and Shottky,[32] one of the authors[17] has written the interaction between the electron and the hole in an insulator as

$$H_{\text{int}}(r) = -\frac{e^2}{r} + \tfrac{1}{2}\sum_{\vec{k}} |\gamma_{\vec{k}}|^2 \times \left( \frac{e^{i\vec{k}\cdot\vec{r}}}{\hbar^2 k^2/2m_e^* + E_{\text{ex}}} + \frac{e^{i\vec{k}\cdot\vec{r}}}{\hbar^2 k^2/2m_h^* + E_{\text{ex}}} + \text{c. c.} \right) + H_{\text{se}}(e) + H_{\text{se}}(h) \ , \tag{4.6}$$

where $\vec{k}$ is the wave vector, $E_{\text{ex}}$ is the exciton energy (i.e., the energy necessary to excite an electron to the first exciton level), $r$ is the separation of the electron from the hole, and $m_e^*$ and $m_h^*$ are the effective masses of the electron and the hole, respectively; $|\gamma_{\vec{k}}|^2$ is given by

$$|\gamma_{\vec{k}}|^2 = (E_{\text{ex}})^2 (4\pi/Vk^2)(\alpha/\mu) \ . \tag{4.7}$$

Here $V$ is the volume of the crystal, and $\alpha/\mu$ is

$$\alpha/\mu = (e^2/2E_{\text{ex}})(1 - 1/\epsilon_0) \ , \tag{4.8}$$

and $\epsilon_0$ is the optical dielectric constant.

The two $H_{\text{se}}$ terms represent the self-energies of the electron and the hole with respect to the electronic polarization, and are given by the second term of expression (4.6) with $\exp(i\vec{k}\cdot\vec{r})$ replaced by − 1. Converting the summation $\sum_{\vec{k}}$ into $[V/(2\pi)^3] \times \int d^3\vec{k}$ and integrating to $k = \pi/a$, one gets

$$H_{\text{int}}(r) = \frac{-e^2}{r} + \frac{e^2}{\pi}\left(1 - \frac{1}{\epsilon_0}\right) \int_0^{\pi/a} dk \left(\frac{\sin kr}{kr} - 1\right) \times \left( \frac{1}{1 + k^2/v_e^2} + \frac{1}{1 + k^2/v_h^2} \right) , \tag{4.9}$$

where $v_e$ and $v_h$ are given by

$$v_i = (2m_i^* E_{\text{ex}}/\hbar^2)^{1/2} \ . \tag{4.10}$$

One may then calculate the expression (4.9) in two approximations: the static and the dynamic approximations. In the former, obtained supposing that $v_e$ and $v_h$ are much smaller than $\pi/a$ and, therefore, replacing the upper limit of the integrand by ∞, one gets, in accord with Haken and Schottky,

$$H_{\text{int}}^d = -(e^2/r) + (e^2/r)(1 - 1/\epsilon_0)[1 - \tfrac{1}{2}(e^{-v_e r} + e^{-v_h r})] - (e^2/r)(1 - 1/\epsilon_0)(v_e + v_h) \ . \tag{4.11}$$

In the latter case, where one supposes $v_i \gg \pi/a$, so that the term $k^2/v_i$ is negligible, one gets

$$H_{\text{int}}^s = -(e^2/r) + (e^2/r)(1 - 1/\epsilon_0)(1 - e^{-2r/a}) - (2e^2/a)(1 - 1/\epsilon_0) \ . \tag{4.12}$$

After observing that the static value for the self-energy agrees closely with the Mott-Littleton (ML) result

$$-e^2(1 - 1/\epsilon_0)[(1/2R_e) + (1/2R_h)] \ ,$$

where $R_e$ and $R_h$ are the ML[33] radii, and that the $r$ dependence of $H_{\text{int}}$ is much closer to the static than to the dynamic result, for large $m^*$ insulators, it was proposed in Ref. 17 that a reasonable approach would be to write $H_{\text{int}}$ as

$$H_{\text{int}} = -(e^2/r) + (e^2/r)(1 - 1/\epsilon_0) \times [1 - \tfrac{1}{2}(e^{-\alpha_e r} + e^{-\alpha_h r})] + H_{\text{se}}(h) + H_{\text{se}}(e) \ , \tag{4.13}$$

where

$$H_{\text{se}}(i) = \tfrac{1}{2} e^2 (1 - 1/\epsilon_0)\alpha_i \ , \tag{4.14}$$

and the parameters $\alpha_i$ are chosen such that the self-energies calculated with the above expression are equal to the ones calculated with ML theory. Values of $\alpha_i$ for different ionic and rare-gas crystals were tabulated in Ref. 17. For argon, one obtains $\alpha_e = \alpha_h = 0.38$ Å$^{-1}$, giving $H_{\text{se}}(e) = H_{\text{se}}(h) = 1.1$ eV. It was then argued that the number $H_s = H_{\text{se}}(h) + H_{\text{se}}(e)$ represents the approximate self-energy corrections that should be subtracted from the one-electron energy gaps in order to obtain optical or experimental gaps; i.e., the conduction bands must be lowered by the value $H_{se}(e)$ and the valence bands raised by the amount $H_{se}(h)$.

Even though the values for the self-energies we have calculated are different from those obtained in Ref. 17, it is evident that we have a striking qualitative agreement. The quantitative differences are not surprising in view of the different physical nature of the initial interactions.

## V. DISCUSSION OF RESULTS AND COMPARISON WITH EXPERIMENT

We have seen that the OPW method is able to give convergent results for the energy bands for insulator crystals. Others had also used this method previously to calculate energy bands in insulators, proving the soundness of the OPW method, in contrast with its original use. In our case, we have seen that, even if the exchange potential is state dependent, OPW is still able to give convergent results.

In the first part of this work we have performed two energy-band calculations without including correlation in order to see how good the results are which one obtains by doing a HF calculation. We have seen that a HF calculation yields bands with an energy gap (~ 17 eV) which is larger than the experimental one, 14.3 eV, whereas a HF calculation including the Slater approximation for the exchange changes appreciably the calculated energy gap (~ 7.6 eV) which now becomes smaller than the experimental one. There are also changes in the structure of the different bands even if this effect is not as large as the first.

It is, therefore, evident that when one performs a calculation including the Slater approximation one obtains results which do not reflect any more than the HF scheme. The Slater approximation is a useful one from the practical point of view, but one should be aware that when one is using it, one cannot claim one is doing a HF calculation.

We have also seen that it is possible to include correlation in an energy-band calculation, and this requires the knowledge of the dielectric function. The energy-band calculation including an approximate treatment of the correlation effects has been shown to give very reasonable results.

TABLE XI. Comparison between Mattheiss results and ours. For more details see Ref. 7.

| State | Energies (in eV)<br>Mattheiss | Our calculation |
|---|---|---|
| $\Gamma_1(1)$ | −31.9736 | −32.6811 |
| $\Gamma_{15}(1)$ | −17.0408 | −13.6371 |
| $\Gamma_1(2)$ | − 3.7264 | 0.0601 |
| $\Gamma_{25}'(1)$ | 2.1488 | 10.3296 |
| $\Gamma_1(2)-\Gamma_{15}(1)$ | 13.3144 | 13.6971 |
| $\Gamma_{25}'(1)-\Gamma_1(2)$ | 5.8752 | 10.2695 |
| $X_5'(1)-X_4'(1)$ | 0.3536 | 1.3446 |
| $X_3(1)-X_1(2)$ | 1.1288 | 2.2347 |
| $\Gamma_{15}(1)-X_4'(1)$ | 0.5576 | 2.0575 |
| $X_1(2)-\Gamma_1(2)$ | 2.5704 | 2.9557 |
| $L_2'(1)-L_3'(1)$ | 0.5304 | 1.8970 |
| $L_2'(2)-L_2(2)$ | 1.6456 | 1.8958 |
| $L_3'(1)-L_2'(1)$ | 0.5984 | 2.3124 |
| $L_1(2)-\Gamma_1(2)$ | 2.6792 | 3.3927 |

Since there has been some previous work done for argon, both from the theoretical and experimental point of view, it is desirable to compare our results with these. Theoretically, our energy bands can be compared with the calculations performed by Knox and Bassani[6] and by Mattheiss.[7] Knox and Bassani used a tight-binding method for the valence bands and the OPW method, in a perturbation approximation, for the conduction bands. There is very little similarity between their bands and the ones we obtained. The reciprocal positions, absolute energies, and details of the bands are different. The main agreement is that both calculations predict $\Gamma_1$ to be the lowest conduction point and $\Gamma_{15}$ to be the highest valence-band point. The band-gap value obtained by Knox and Bassani is 12.4 eV.

A better comparison can be made between Mattheiss's calculation and ours. The method used by Mattheiss has been APW. Table XI shows a comparison of some energy values calculated by Mattheiss with ours. There is a generally satisfactory agreement. The order of the bands is the same for the valence states and the lowest conduction states, whereas there are some discrepancies for higher conduction states. In our case, the *d* conduction states are higher; the width of the valence bands is in his case 0.7 eV, whereas in our case it is 2.3 eV. The band gap obtained by Mattheiss is 13.3 eV as compared with our 13.7 eV.

Experimentally, solid argon has been studied recently by many people.[31,34–37] Baldini[31] has studied the optical properties of solid krypton, xenon, and argon. Other experiments on solid argon have been done by Bostanjoglo and Schmidt[34] using light-absorption and fast-electron techniques. A very recent measurement of the reflectance of solid argon at 20 °K in the energy range from 10–30 eV using synchrotron radiation has been performed by Haensel *et al.* Results of such an experiment are given in Fig. 7.

We do not discuss here the excitonic structure in argon and how it is possible to explain it. We only say that from the position of the different ex-

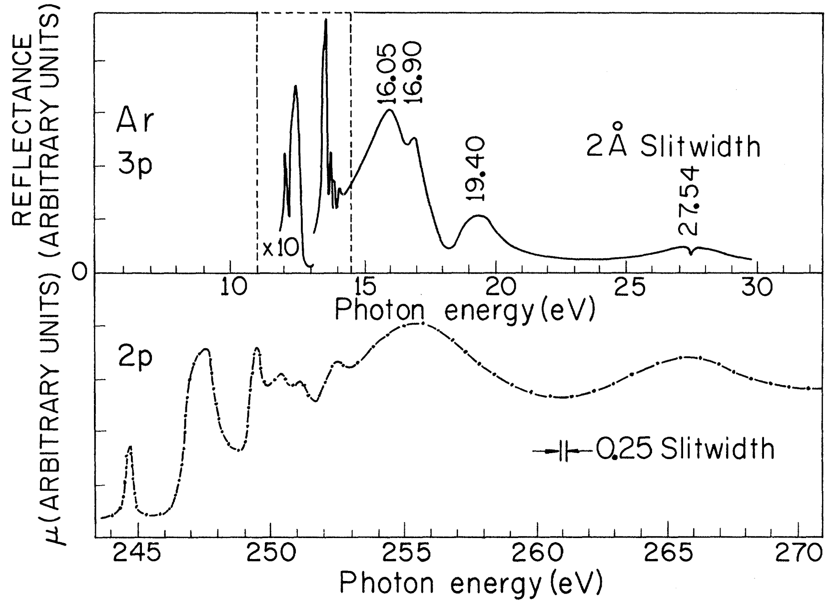

FIG. 7. Reflectance spectrum for solid argon after Haensel *et al.*, Ref. 37.

citon peaks it is possible to determine, in a good approximation, the value of the energy gap. From the above experiments, one deduces a gap of about 14.3 eV. The value predicted by our energy bands is about 13.7 eV. The agreement is, therefore, good. We remember that the value obtained from the HF band calculation without correlation was 17.2 eV, so that we really see how the inclusion of correlation is necessary in order to get agreement with experiment. The width of the valence $p$-like bands predicted by our calculation is about 2.3 eV. Unfortunately, there are not experimental data available on this and therefore it would be useful to perform some experiments similar to that done by Parratt and Jossem[38] for KCl. Deslattes[39] has measured emission spectra for gaseous argon. A similar experiment using solid argon, if possible, could give useful information.

The experiment performed by Haensel *et al.* is the only one where transitions are shown occurring above the band-transition edge. Phillips[40] has shown that it is possible to explain the ultraviolet-energy-region spectra in terms of energy bands. We can then try to interpret this structure. Figure 7 shows two peaks at 16.05 and 16.90 eV. Our energy bands predict two possible transitions, $X_1 \to X_5'$ and $L_1 \to L_3'$, at 16.48 and 16.62 eV, respectively. A correspondence between our predictions and the two experimental peaks is, therefore, possible. Figure 7 shows another transition occurring at 19.40 eV, which could correspond to our $X_3 \to X_4'$ which occurs at 20.06 eV. Finally, the peak at 27.54 eV could correspond to the transition $\Gamma_{12} \to \Gamma_{15}$ (predicted 26.5 eV). An interesting question could be why there are no transitions shown to occur between 19.40 and 27.54 eV, whereas our bands predict some possible transitions in that region. One possible answer to this question could be that the intensity of these transitions is too weak. However, some other experiment performed in this range of energy could be useful to clarify this point.

We have, therefore, seen how it is possible to obtain reasonable energy bands for insulators when the correlation effects are taken into account, whereas a pure HF calculation does not compare well with experiment. We have also seen that Fowler's treatment of the effect of electronic polarization is fundamentally correct. It could be useful to perform energy-band calculations in other insulators where the dielectric constant is greater in order to confirm the above conclusions. Alkali-halide crystals look promising in this sense. Other pure HF calculations could be useful in order to determine the limits of the HF approximation.

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## APPENDIX: TREATMENT OF EXCHANGE POTENTIAL

We can write the exchange operator in the form

$$\langle x | V_{\mathrm{ex}} | \psi \rangle = -e^2 \int \sum_{\vec{\mathrm{k}}n} \frac{f_{\vec{\mathrm{k}}n}(x)\, f^*_{\vec{\mathrm{k}}n}(x')\, \psi(x')\, dx'}{|\vec{\mathrm{r}} - \vec{\mathrm{r}}\,'|} . \tag{A1}$$

Since we work in a.u. we will have in the following $e^2 = 2$. It is our purpose to calculate the matrix elements $\langle \vec{p} | V_{\text{ex}} | \vec{p}' \rangle$, where $p$'s are plane-wave momenta. According to the argument presented in the text, we now assume that the functions $f_{\vec{k}n}$ are given by the expression

$$f_{\vec{k}n} = N^{-1/2} \sum_\mu e^{i\vec{k}\cdot\vec{R}_\mu} u_{nlm}(\vec{r} - \vec{R}_\mu) S(\sigma) \quad , \tag{A2}$$

where $u_{nlm}(\vec{r} - \vec{R}_\mu)$ represents the $nlm$ orbital of the atom located at $\vec{R}_\mu$ in the unit cell; thus we have

$$\langle \vec{p}' | V_{\text{ex}} | \vec{p} \rangle = -2 \int\int d^3r \, d^3r' \times \sum_{\vec{k}n} \frac{f_{\vec{k}n}(\vec{r}) f_{\vec{k}n}(\vec{r}') e^{-i\vec{p}\cdot\vec{r}} e^{i\vec{p}\cdot\vec{r}'}}{|\vec{r} - \vec{r}'|} \quad . \tag{A3}$$

Because of crystal symmetry, $\vec{p}' = \vec{p} + \vec{K}$, where $\vec{K}$ is a reciprocal-lattice vector. We now write

$$1/|\vec{r} - \vec{r}'| = \int [d^3q/(2\pi)^3] (4\pi/q^2 v) e^{i(\vec{r}-\vec{r}')\cdot\vec{q}} \, . \tag{A4}$$

Carrying out the sums over $\vec{k}$, $\mu$, and $\mu'$ we get

$$\langle \vec{p}' | V_{\text{ex}} | \vec{p} \rangle = \frac{-2}{\Omega} \int \frac{d^3\vec{q}}{(2\pi)^3} \frac{4\pi}{q^2} \sum_{nlm} \left[ \int d^3\vec{r} \, e^{-i(\vec{p}'+\vec{q})\cdot\vec{r}} u_{nlm}(\vec{r}) \times \int d^3r' e^{i(\vec{p}+\vec{q})\cdot\vec{r}'} u^*_{nlm}(\vec{r}') \right] . \tag{A5}$$

Following Woodruff, since core and valence shells are filled, we have

$$\sum_m \frac{1}{\Omega} \int d^3r \, e^{-i(\vec{p}'+\vec{q})\cdot\vec{r}} u_{nlm}(\vec{r}) \int d^3r' e^{i(\vec{p}+\vec{q})\cdot\vec{r}'} u^*_{nlm}(\vec{r}') = A_{nl}(|\vec{p}'+\vec{q}|) A^*_{nl}(|\vec{p}+\vec{q}|) P_l(\cos\theta) \quad ; \tag{A6}$$

where

$$\cos\theta = (\vec{p}+\vec{q}) \cdot (\vec{p}'+\vec{q}) / |\vec{p}+\vec{q}| \, |\vec{p}'+\vec{q}| \quad , \tag{A7}$$

$P_l$ is the Legendre polynomial, and

$$A_{nl}(|\vec{K}|) = \Omega^{-1/2} \int u_{nlm}(\vec{r}) e^{i\vec{k}\cdot\vec{r}} d^3r = [4\pi(2l+1)/\Omega]^{1/2} (i)^l \int_0^\infty r P_{nl}(r) j_l(kr) \, dr \, ; \tag{A8}$$

where we have written

$$u_{nlm}(r) = Y_l^m(\theta, \varphi) P_{nl}(r)/r \quad .$$

Here, the $j_l(kr)$ are the spherical Bessel functions. Thus we get

$$\langle \vec{p}' | V_{\text{ex}} | \vec{p} \rangle = -2 \sum_{n,l} \int \frac{d^3\vec{q}}{(2\pi)^3} A_{nl}(|\vec{p}+\vec{q}|) A^*_{nl}(|\vec{p}'+\vec{q}|) \times P_l(\cos\theta) \cdot \frac{4\pi}{q^2} \, . \tag{A9}$$

In order to make the calculations practically feasible, it is good to have analytical expressions for $A_{nl}$ so that we are left with only the integral in $q$. In order to do this, we assume analytical radial wave functions of the form given by Watson and Freeman, i.e.,

$$P_{nl}(r) = \sum_j C^j_{nl} R^l_j(r) \quad , \tag{A10}$$

and the basic functions $R^l_j(r)$ are of the form

$$R^l_j = N_j r^{(l+A_j+1)} e^{-Z_j r} \quad ; \tag{A11}$$

$N_j$ is a normalization constant which can be expressed in terms of the other quantities as

$$N_j = [(2Z_j)^{2l+2A_j+3} / (2l + 2A_j + 2)!]^{1/2} \quad . \tag{A12}$$

Using (A9), we have

$$A_{nl}(k) = \left( \frac{4\pi(2l+1)}{\Omega} \right)^{1/2} (i)^l \sum_{j=1}^{i_m} C^j_{n1} N_j (-1)^{A_j+1} \times \frac{d^{(A_j+1)}}{dZ_j^{(A_j+1)}} \left( \frac{(2k)^l l!}{(k^2 + Z_j^2)^{l+1}} \right) = \sum_{\mu=1}^{\mu_m} B^{nl}_\mu \frac{k^l}{(k^2 + Z_\mu^2)^{m_\mu+1}} \quad , \tag{A13}$$

where the coefficients $B^{nl}_\mu$ depend on $C^j_{nl}$, $N_j$, $C_j$, and $A_j$. We can, therefore, write for the exchange matrix elements

$$\langle |\vec{p}'| V_{\text{ex}} |\vec{p}\rangle = -2 \sum_{n,l} \sum_{\mu=1}^{\mu_m} \sum_{\nu=1}^{\nu_m} B^{nl}_\mu B^{nl*}_\nu \int \frac{d^3\vec{q}}{(2\pi)^3} \frac{4\pi}{q^2} \times \frac{|\vec{p}+\vec{q}|^l}{(|\vec{p}+\vec{q}|^2 + Z_\mu^2)^{m_\mu+1}} \frac{|\vec{p}'+\vec{q}|^l}{(|\vec{p}'+\vec{q}|^2 + Z_\nu^2)^{n_\nu+1}} P_l(\cos\theta) = \sum_{n,l} \sum_\mu \sum_\nu B^{nl}_\mu B^{nl}_\nu T^l_{\mu\nu} \quad , \tag{A14}$$

where

$$T^l_{\mu\nu} = -2 \int \frac{d^3q}{(2\pi)^3} \frac{4\pi}{q^2} \frac{|\vec{p}+\vec{q}|^l}{(|p+q|^2 + Z_\mu^2)^{n_\mu+1}} \times \frac{|\vec{p}'+\vec{q}|^l}{(|p'+q|^2 + Z_\nu^2)^{n_\nu+1}} P_l(\cos\theta) \quad . \tag{A15}$$

This is the essential integral to be evaluated. Since this integral is very complicated due to the angular dependence in every term of it, the first thing one hopes to see is if it is possible to separate the angular dependence from the radial dependence in every term in the above expression. This is the idea of Brinkman.[28] We first consider the case $l = 0$. From (A15) we have

$$T_0^{\mu\nu} = T_s^{\mu\nu} = -2 \int \frac{d^3\vec{q}}{(2\pi)^3} \frac{4\pi}{q^2} \frac{1}{(|\vec{p}+\vec{q}|^2 + Z_\mu^2)^{m_\mu+1}} \times \frac{1}{(|\vec{p}'+\vec{q}|^2 Z_\nu^2)^{m_\nu+1}} \quad . \tag{A16}$$

Now we can write

$$\frac{1}{(|\vec{p}+\vec{q}|^2 + Z_\mu^2)^{m_\mu+1}} = \frac{1}{(2pq)^{m_\mu+1}} \frac{(-1)^{m_\mu}}{m_\mu!}$$

$$\times \left( \frac{d^{m_\mu}}{dx^{m_\mu}} \frac{1}{x+\cos y} \right) , \tag{A17}$$

where

$$x = (p^2 + q^2 + Z_\mu^2)/2pq , \quad \cos y = \vec{p}\cdot\vec{q}/|\vec{p}|\ |\vec{q}| . \tag{A18}$$

We now use the Heine's formula

$$\frac{1}{k+z} = \sum_{j=0}^{\infty} (-1)^j (2j+1) P_j(z)\, Q_j(x) . \tag{A19}$$

Expression (A19) is valid for any point $z = \xi + i\eta$ which is inside the ellipse drawn through the point $x$ and having foci at the points ±1. We have, therefore, after some manipulations,

$$T_s^{\mu\nu} = \sum_{j=0}^{\infty} -\frac{4(2j+1)}{\pi} P_j(\cos\theta) \int_0^\infty dq \frac{(-1)^{m_\mu}}{(2pq)^{m_\mu+1}}$$

$$\times \frac{d^{m_\mu}}{dx^{m_\mu}} Q_j(x) \frac{1}{m_\mu !} \frac{1}{(2p'q)^{m_\nu+1}}$$

$$\times \frac{(-1)^{m_\nu}}{m_\nu !} \frac{d^{m_x}}{dx'^{m_\nu}} Q_j(x') , \tag{A20}$$

where $\cos\theta = \vec{p}\circ\vec{p}'/|\vec{p}|\ |\vec{p}'|$. If we define

$$y_\mu = p^2 + q^2 + Z_\mu^2 , \qquad x_\mu = 2pq ;$$

$$y_\nu = p'^2 + q^2 + Z_\nu^2 , \qquad x_\nu = 2p'q ;$$

we can write

$$T_s^{\mu\nu}(p,p') = \sum_{j=0}^{\infty} P_j(\cos\theta) S_j^{\mu\nu}(p,p') , \tag{A21}$$

where

$$S_j^{\mu\nu} = \frac{-4(2j+1)}{\pi} \int_0^\infty dq \frac{H_j^{m_\mu}(x_\mu, y_\mu)}{m_\mu !} \frac{H_j^{m_\nu}(x_\nu, y_\nu)}{m_\nu !} , \tag{A22}$$

$$H_j^{m_\mu}(x_\mu, y_\mu) = \frac{(-1)^{m_\mu}}{x_\mu^{m_\mu+1}} \frac{d^{m_\mu}}{d(y_\mu/x_\mu)^{m_\mu}} Q_j(y_\mu/x_\mu) , \tag{A23}$$

and similarly for $H_j^{m_\nu}(x_\nu, y_\nu)$.

We, therefore, have

$$\langle \vec{p}'|\, V_{\text{ex}}^{(s)} |\vec{p}\rangle = \sum_{j=0}^{\infty} P_j(\cos\theta) S_j^0(p,p') , \tag{A24}$$

where

$$S_j^0(p,p') = \sum_n \frac{-4(2j+1)}{\pi} \int_0^\infty dq \left( \sum_\mu D_\mu^{n0} H_j^{n_\mu}(x_\mu, y_\mu) \right)$$

$$\times \left( \sum_\nu D_\nu^{n0} H_j^{n0}(x_\nu, y_\nu) \right) , \tag{A25}$$

and $D_\mu^{n0} = B_\mu^{n0}/m_\mu !$. The sum over $n$ means sum over all $s$ states.

For states different than $s$ states, i.e., for $p$ and $d$ states for which $l = 1, 2$ (in our case we have only $p$ states), we can show that we have expressions similar to the $l = 0$ case. In effect, for $l = 1$ we see that

$$|\vec{p}+\vec{q}|\ |\vec{p}'+\vec{q}|\ P_1(\cos\theta) = (\vec{p}+\vec{q})\cdot(\vec{p}'+\vec{q}) . \tag{A26}$$

Using the relation

$$\frac{\vec{p}\cdot\vec{q}}{(|\vec{p}+\vec{q}|^2 + Z_\mu^2)^{m_\mu+1}} = \frac{1}{2}\left( \frac{1}{(|\vec{p}+\vec{q}|^2 + Z_\mu^2)^{m_\mu}} - \frac{(p^2+q^2+Z_\mu^2)}{(|\vec{p}+\vec{q}|^2 + Z_\mu^2)^{m_\mu+1}} \right) , \tag{A27}$$

we can treat the angular integration in the same way as in the $l = 0$ case, so that, as a result, we have the same type of radial integral as $S_j^0$ but several of them for $p$ states. We then obtain, in general,

$$\langle \vec{p}|\, V_{\text{ex}} |\vec{p}'\rangle = \sum_{j=0}^{\infty} P_j(\cos\theta) S_j(p,p') , \tag{A28}$$

where $S_j(p,p')$ contains a sum over all the atomic states. The one-dimensional integral involved into the $S_j(p,p')$ has been carried out numerically. An important point involves the question of how many terms in the series expansion (A28) one should include in order to obtain a good estimation of $\langle\vec{p}|\, V_{\text{ex}} |\vec{p}'\rangle$. One observes that the convergence of (A28) depends on three factors: (a) the type of atomic states involved in the summation, (b) the extension of these states in real space, and (c) the magnitude of $p$ and $p'$. Brinkman, in his original calculation for silicon, included five terms in the above expansion. In our case, these terms are not enough (i) because we have many plane waves so that $p$ and $p'$ can become very large, and (ii) because we are including in our exchange all the atomic states, whereas Brinkman included only core states. It is, therefore, necessary to include more terms. In our calculation we have included another two terms because the further addition of another two terms does not produce any substantial variation in the results (less than 0.001 eV).

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[1] A complete list of references on this topic would be impossible. A large amount of information about the experimental situation in argon can be found in Refs. 31, 34–37.

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