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Hartree-Fock Band Structure and Optical Gap in Solid Neon and Argon

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A method closely related to the classical augmented-plane-wave (APW) method is developed which treats in a nearly exact way the Hartree-Fock exchange in the case of crystals having deeply bound and filled valence bands. Band-structure calculations have been performed for solid neon and argon. The main conclusions of Lipari and Fowler for argon are confirmed: a too large gap which proves the influence of correlation in these insulators, large valence bands, and change in the shift between conduction bands without significant modification of their internal structure. Yet, we note that we found a smaller separation between s and d bands than Lipari and Fowler. The value of the Hartree-Fock energy gap is physically related to the experimental one in terms of the correlation energies involved in a transition from a localized valence state to an extended conduction state. Using atomic correlation values for the valence state and previous results for the polarization in solid rare gases, a good qualitative agreement is found.

I. INTRODUCTION

Different band-structure calculations on solid neon and argon have been performed during the last ten years paralleling the progress in experimental measurements. Knox and Bassani,[1] using a perturbation approximation to the orthogonalized-plane-wave (OPW) method, and two years later Mattheiss,[2] using the augmented-plane-wave (APW) method, have given the dispersion curves $E(k)$ for argon. These authors introduced the exchange potential by means of Slater's free-electron approximation. Their results were in qualitative agreement with experiment, though there were important quantitative differences.

The band structures of Ne, Ar, Kr, and Xe can also be found in a paper by Rössler.[3] The calculation for Ar up to Xe was based on the relativistic formulation of the Green's-function method, but was nonrelativistic for neon. The exchange was also taken into account by an approximate local potential, and the constant potential outside the "muffin tin" was chosen to obtain the experimental value of the gap between conduction and valence bands. The general features of the band structure of Ar were similar to those found in previous calculations.

The problem of the band structure of Ar has been recently considered by Lipari and Fowler.[4] Two types of new OPW calculations were made: a Hartree-Fock (HF) calculation with the exchange potential treated in a nearly exact manner, and a calculation where the correlations were included by a rather complicated procedure. The only agreement between the HF calculation and the previous results was the internal structure of the bands. But the energy gap found by Lipari and Fowler is much larger than previously calculated gaps and experimental gaps. Similarly, the separation between s and d bands is larger in the HF case, and the valence band is wider. Finally, the second calculation of Lipari and Fowler proved that the influence of correlations is very strong.

Thus the situation is that the gap, as calculated by Knox and Bassani and then by Mattheiss with statistical exchange, is in better agreement with experiment than the nearly exact HF gap of Lipari and Fowler. To explain this fact, we note that the comparison between the optical gap and difference of eigenvalues calculated in a statistical exchange potential is incorrect since, in this case, Koopmans's theorem fails. Slater[5] has pointed out that Koopmans's corrections are certainly significant when the optical transition occurs from an atomic-like localized state to an extended crystal state. It can be expected that a calculation with Kohn and Sham's statistical exchange and Koopman's correction would give a larger gap than previous values obtained in Refs. 1 and 2. Furthermore, it may be assumed that the statistical approximation to exchange acts as though it included correlation effects. For all these reasons, we think, as do Lipari and Fowler, that it is important to solve the HF equations as exactly as possible. Only from these results will it be possible, by adding adequate correlation corrections, to interpret experimental measurements.

In Sec. II, we describe a method, closely related to the well-known APW method, to treat the HF equations in solid rare gases. We give the results for neon and argon and compare them with those of Lipari and Fowler in Sec. III. Correlation effects are discussed in Sec. IV, in relation to the interpretation of the experimental gap.

II. METHOD TO SOLVE HF EQUATIONS IN SOLID RARE GASES

The physical background of the method is that, in solid rare gases, the highest occupied levels are tight enough to have a very pronounced atomiclike character. So a good Coulomb crystal potential can be obtained from Bloch sums built from atomiclike wave functions. This potential is then introduced in the equations of a band-structure-calculation method: We have chosen the APW method. The approximation used for the exchange terms is very similar: All the wave functions appearing in these terms are taken as Bloch sums of atomiclike orbitals, except the wave function of the state we are calculating which is an expansion in APW.

As a first step, we set up the atomiclike orbitals φ_{nlm} used to construct the Bloch sums $\phi_{nlm,i}$:

$$\begin{aligned} \varphi_{nlm}(\vec{r}) &= P_{nl}(r)\, Y_l^m(\hat{r}), \\ \phi_{nlm,i}(\vec{r}) &= \frac{1}{N^{1/2}} \sum_a e^{i\vec{k}_i\cdot\vec{X}_a}\, \varphi_{nlm}(\vec{r}-\vec{X}_a). \end{aligned} \tag{1}$$

We assume that there is no mixing of the quantum numbers n and l between one occupied band and another. N is the number of unit cells in the crystal and $\vec{X}_a$ a translation vector of the direct lattice. The orbitals φ_{nlm} are normalized in a sphere of radius S_B of same volume Ω as the unit cell (Wigner-Seitz sphere). The resulting density at radius S_B is assumed to be negligible; thus orbitals located on different lattice sites do not overlap. The variational principle, applied to the total energy obtained from these wave functions, gives the system of coupled equations:

$$\left(-\frac{\Delta_r}{2} + U(r) + \frac{l(l+1)}{2r^2} - E_{nl}\right)P_{nl} = \sum_{n'l'} \sum_L C^L(l0, l'0) \times P_{n'l'}(r) \int_\Omega \frac{r_<^L}{r_>^{L+1}}\, P_{n'l'}(r')\, P_{nl}(r')\, r'^2\, dr', \tag{2}$$

with

$$U(r) = -\frac{Z}{r} + \int_\Omega \frac{1}{r_<} \sum_{nlm} P_{nl}^2(r')\, r'^2\, dr',$$

$$C^L(l0, l'0) = \left(\frac{4\pi(2l'+1)}{(2l+1)(2L+1)}\right)^{1/2} \int Y_L^{0*}(\hat{\sigma})\, Y_l^0(\hat{\sigma})\, Y_{l'}^0(\hat{\sigma})\, d\hat{\sigma}.$$

System (2) is exactly the system of HF equations for a complete-shell atom, with a single difference on the integration volume which is limited here to a sphere of radius S_B.

We now have the atomiclike orbitals needed to calculate the crystal "muffin-tin potential" and the exchange integrals. The Coulomb part $V(r)$ of the potential to be used in the band-structure calculations is equal to the potential $U(r)$ [resulting from the self-consistent solution of (2)] inside the APW sphere surrounding each atom. Outside the APW sphere, the crystal potential is constant and equal to the mean value of the potential $U(r)$. The radius S_A of the APW spheres is chosen as usual, so that they just touch at the cell boundaries:

$$V = U(r)\ , \qquad 0 \le r \le S_A$$

$$V = V_0 = \frac{1}{\Omega - \frac{4}{3}\pi S_A^3} \int_{S_A}^{S_B} U(r)\, d\vec{r}, \quad S_A \le r.$$

The total charge included in each APW sphere is approximately zero, so V_0 is very small.

The second step of the method is the more refined description of the electronic states we want to calculate in the valence and conduction bands. The wave functions ψ_j are expanded in APW's f_p^j of wave vectors $\vec{k}_j + \vec{K}_p$, where $\vec{k}_j$ is the reduced wave vector and $\vec{K}_p$ is a vector of the reciprocal lattice.[6] Inside the APW sphere, one has

$$\begin{aligned} \psi_j &= \sum_p C_p^j f_p^j = \sum_{\lambda\mu} d_{\lambda\mu}^j\, R_\lambda^j(r)\, Y_\lambda^\mu(\hat{r}), \\ d_{\lambda\mu}^j &= \sum_p 4\pi\, i^\lambda\, J_\lambda(|k_j + K_p|\, S_A)\, \frac{1}{R_\lambda^j(S_A)}\, Y_\lambda^{\mu*}(k_j + K_p). \end{aligned} \tag{3}$$

The radial part of the APW for state j and angular momentum λ is R_λ^j, and J_λ is the spherical Bessel function of the same momentum. Outside the sphere, the APW f_p^j reduces to a plane wave:

$$f_p^j = e^{i(\vec{k}_j + \vec{K}_p)\cdot\vec{r}}\ .$$

The main problem we are dealing with is the treatment of the exchange energy for the state j, which is

$$-\sum_{j'} \delta(m_{s_j}, m_{s_{j'}}) \iint \psi_{j'}^*(\vec{r}_1)\, \psi_j(\vec{r}_1)\, \frac{1}{r_{12}}\, \psi_j^*(\vec{r}_2) \times \psi_{j'}(\vec{r}_2)\, d\vec{r}_1 d\vec{r}_2\ ,$$

where $\delta(m_{s_j}, m_{s_{j'}}) = 1$ if the spins of electrons j and j' are parallel, and zero otherwise. The summation is on all the occupied states. We said above that our approximation to calculate such an integral will be to replace the exact functions $\psi_{j'}$, by the Bloch functions $\phi_{nlm,j'}$. The exchange integral becomes

$$E_X^j = -\sum_{nlm,i} \delta(m_{s_i}, m_{s_j}) \iint \phi^*_{nlm,i}(\vec{r}_1)\, \psi_j(\vec{r}_1)\, \frac{1}{r_{12}}\, \psi_j^*(\vec{r}_2) \times \phi_{nlm,i}(\vec{r}_2)\, d\vec{r}_1\, d\vec{r}_2 . \quad (4)$$

The integral on the whole crystal can be broken up into integrals over unit cells by the change of coordinates

$$\vec{r}_1 = \vec{\rho}_1 + \vec{X}_a, \quad \vec{r}_2 = \vec{\rho}_2 + \vec{X}_b,$$

and the use of the translational properties of the wave functions,

$$E_X^j = -\frac{1}{N} \sum_{nlm,i} \delta(m_{s_i}, m_{s_j}) \sum_{ab} e^{-i(\vec{k}_i - \vec{k}_j)\cdot(\vec{X}_a - \vec{X}_b)} \iint \varphi^*_{nlm} \times (\vec{\rho}_1)\, \psi_j(\vec{\rho}_1)\, \frac{1}{|\vec{\rho}_{12} + \vec{X}_a - \vec{X}_b|}\, \psi_j^*(\vec{\rho}_2)\, \varphi_{nlm}(\vec{\rho}_2)\, d\vec{\rho}_1\, d\vec{\rho}_2 .$$

The integration is now to be performed over the unit cell surrounding the origin. As all the occupied bands are filled, the sum

$$\textstyle\sum_i \delta(m_{s_i}, m_{s_j})\, e^{-i\vec{k}_i\cdot(\vec{X}_a - \vec{X}_b)}$$

vanishes unless $\vec{X}_a = \vec{X}_b$; in this case, its value is N. The exchange energy reduces to

$$E_X^j = -\sum_{nlm} \iint_\Omega \varphi^*_{nlm}(\vec{\rho}_1)\, \psi_j(\vec{\rho}_1)\, \frac{1}{\rho_{12}}\, \psi_j^*(\vec{\rho}_2) \times \varphi_{nlm}(\vec{\rho}_2)\, d\vec{\rho}_1\, d\vec{\rho}_2 .$$

As the functions φ_{nlm} are deeply bound, the region outside the APW sphere in the cell is expected to give a very small contribution to E_X^j. We shall neglect it and calculate the integral over the volume of the APW sphere only.

Recalling that the shells n, l are closed, we have

$$\sum_m \varphi^*_{nlm}(\vec{\rho}_1)\, \varphi_{nlm}(\vec{\rho}_2) = \frac{2l+1}{4\pi} P_{nl}(\rho_1)\, P_{nl}(\rho_2)\, \mathcal{P}_l(\rho_1 \cdot \rho_2),$$

where $\mathcal{P}_l$ is the Legendre polynomial of order l. This result, together with the usual expansion of $1/\rho_{12}$, gives the following expression for E_X^j:

$$E_X^j = -\sum_{nl} \frac{2l+1}{4\pi} \iint_{S_A} P_{nl}(\rho_1)\, \psi_j(\vec{\rho}_1) \sum_L \frac{\rho_<^L}{\rho_>^{L+1}}\, \mathcal{P}_l(\rho_1 \cdot \rho_2) \times \mathcal{P}_L(\rho_1 \cdot \rho_2)\, P_{nl}(\rho_2)\, \psi_j^*(\vec{\rho}_2)\, d\vec{\rho}_1\, d\vec{\rho}_2 .$$

Using the well-known expansion of a product of Legendre polynomials,

$$E_X^j = -\sum_{nl} \sum_L \sum_{l'm'} \frac{2l+1}{2l'+1}\, c^L(l0, l'0) \iint_{S_A} P_{nl}(\rho_1)\, \psi_j(\vec{\rho}_1) \times \frac{\rho_<^L}{\rho_>^{L+1}}\, Y_{l'}^{m'*}(\hat{\rho}_1)\, Y_{l'}^{m'}(\hat{\rho}_2)\, P_{nl}(\rho_2)\, \psi_j^*(\vec{\rho}_2)\, d\vec{\rho}_1\, d\vec{\rho}_2 ,$$

and then the expansion (3) of the function ψ_j,

$$E_X^j = -\sum_{nl} \sum_{l'm'} \sum_L c^L(l0, l'0)\, d^{j*}_{l'm'}\, d^j_{l'm'} \iint_{S_A} P_{nl}(\rho_1)\, R^j_{l'}(\rho_1) \times \frac{\rho_<^L}{\rho_>^{L+1}}\, P_{nl}(\rho_2)\, R^j_{l'}(\rho_2)\, \rho_1^2\, d\rho_1\, \rho_2^2\, d\rho_2 . \quad (5)$$

This formula shows that the exchange operator induces coupling between crystal states of the same angular momentum only.

The exchange energy (5) is added to the kinetic and Coulomb energies in the state j; the variational principle is then applied, together with the normalization condition, and the following equations are obtained:

(a) When the radial parts of the expansion (3) are varied,

$$\left(-\frac{\Delta_r}{2} + V(r) - V_0 + \frac{l(l+1)}{2r^2} - E_j\right) R_l^j(r) = \sum_{n'l'} \sum_L c^L(l0, l'0) \times P_{n'l'}(r) \int_{S_A} \frac{\rho_<^L}{\rho_>^{L+1}}\, R_l^j(\rho')\, P_{n'l'}(\rho')\, \rho'^2\, d\rho' . \quad (6)$$

They show that expansion (3) is a solution of the one-electron equation inside the APW sphere.

(b) Unchanged APW equations are obtained when the coefficients d^j_{lm} are varied. The matrix elements are identical to those given in Refs. 6 and 7, the only difference being that the radial parts needed to calculate the logarithmic derivatives must be solutions of Eq. (6) instead of the original homogeneous equation with local exchange potential. It can easily be shown that different states of the same reduced wave vector remain orthogonal.

To summarize this section, we shall say that when the occupied bands of a crystal are filled and tightly bound, a nearly exact treatment of the HF exchange, but without iterations toward self-consistency, can be performed using the APW scheme. Later we plan to apply this method to ionic crystals as well.

III. PRACTICAL ASPECTS OF METHOD AND RESULTS FOR Ne AND Ar

The method is expected to work for all the solid rare gases, but we have decided to restrict our calculations to neon and argon to avoid a relativistic treatment. Both lattices are fcc with constants $a = 8.542$ (a.u.) for neon and $a = 10.03$ (a.u.) for argon.

The preliminary work has been to compute the self-consistent solution of (2) which gives the atom-

TABLE I. Eigenvalues for the core atomiclike wave functions (Ry).

State	Neon	Argon
1*s*	−65.5261	−237.179
2*s*	−3.84750	−24.6041
2*p*	−1.68923	−19.1028
3*s*	⋯	−2.52642
3*p*	⋯	−1.15816

iclike wave functions needed to calculate the Coulomb potential and the exchange terms. Table I shows the results for the eigenvalues E_{nl} of these equations, expressed in rydbergs, and with the origin chosen so that the Coulomb potential $U(r)$ vanishes at $r=S_B$. The boundary condition used for the integration was an exponential decay at radius S_B. Our assumption of a very small density at this radius was satisfied: The value of the ratio (maximum density/density at radius S_B) was found to equal 153 for the 2*p* state in neon and 34 for the 3*p* state in argon.

The muffin-tin Coulomb potential was then computed. The constant potential outside the APW sphere is very small in both cases: $V_0=-0.00014$ Ry in neon and $V_0=-0.00048$ Ry in argon.

To carry out the APW calculations of the electronic crystal states, the logarithmic derivatives of the radial parts R_l^j must be computed. Equation (6), involving only one radial part, is solved by iteration. For the low angular momenta ($l=0,1,2$), a relative precision of 10^{-6} on the logarithmic derivatives was not obtained with less than ten iterations. For the higher values of l, the convergence was faster and four iterations were sufficient.

The results obtained for the valence and conduction bands are shown in Table II. One-electron energies are given in rydbergs for points of high symmetry Γ, X, L, K. The values are relative to a zero potential outside the APW spheres. Concerning the convergence properties, our secular determinant is similar to the classical APW determinant. It was checked that the given eigenvalues converged with an expansion in orbital quantum number up to $l=10$. The eigenvalues at points Γ_{15} (valence band), Γ_1 and Γ'_{25} (conduction bands) for increasing dimensions of the basis set are shown in Table III. The greatest error due to lack of convergence could be 2×10^{-4} Ry on the levels of Table II.

We come now to the discussion of the results (see Figs. 1 and 2). We first note that the 2*p* band in Ne and the 3*p* band in Ar have the same internal structure. For these valence bands, the bandwidth is 0.036 Ry (0.495 eV) in Ne and 0.089 Ry (1.212 eV) in Ar. We cannot compare our value in Ne with the result of Rössler,[3] who did not give any number. Mat-

TABLE II. Energies of high-symmetry states in neon and argon (values in Ry).

		Neon			Argon		
State	2*p* bands	Conduction bands		3*p* band	Conduction bands		
Γ_1		0.1961			0.2448		
Γ'_2		1.6056			1.1292		
Γ'_{25}		1.5294			0.8563		
Γ_{12}					1.0777		
Γ_{15}	−1.6720	1.8223		−1.1164	1.3398		
X_1		0.6755	1.6902		0.4346	1.4092	
X_3		1.0210			0.5822		
X'_4	−1.7058	0.7479		−1.1997	0.7488		
X'_5	−1.6844	1.3111		−1.1491	1.1107		
L_1		0.6431			0.4768	1.3560	
L'_2	−1.7084	0.5821	1.4969	−1.2053	0.5963	1.0805	
L_3		1.4119			0.8111	1.2412	
L'_3	−1.6911	1.8053		−1.1285	1.4438		
K_1	−1.6916	0.6984	1.4033	−1.1672	0.4957	0.6035	1.0372
K_2					1.2063		
K_3	−1.6987	0.7899		−1.1839	0.7051		
K_4	−1.6805	1.3368		−1.1393	0.9631		

TABLE III. Convergence of the eigenvalues at Γ_{15}, Γ_1, and Γ'_{25} when the dimension of the basis set (first column) increases.

Dimension	Neon $\Gamma_1(s)$	Neon $\Gamma_{15}(p)$	Neon $\Gamma'_{25}(d)$	Argon $\Gamma_1(s)$	Argon $\Gamma_{15}(p)$	Argon $\Gamma'_{25}(d)$
15	0.196 12	−1.670 96	1.529 62	0.244 86	−1.113 69	0.858 70
27	0.196 10	−1.671 91	1.529 39	0.244 81	−1.116 14	0.856 33
51	0.196 10	−1.671 99	1.529 38	0.244 81	−1.116 35	0.856 20

theiss, using the APW method with Slater exchange, found a twice-narrower $3p$ bandwidth of 0.044 Ry (0.598 eV) in Ar: It can be reasonably expected that the HF exchange should give a larger valence band than the statistical exchange. Lipari and Fowler also found a wide valence band of approximately 3 eV, which is much larger than ours. This important discrepancy between two HF calculations needs an explanation; we shall discuss it later.

According to the previous curves of Rössler, using Green's-function method and statistical exchange, the HF conduction bands in solid Ne look like nearly free-electron bands. But there is no more than this qualitative agreement with our results: The ordering of the levels at point Γ is different, and so is the relative location of the various states at points K and X.

Lipari and Fowler have extensively discussed their HF results on argon in relation to the results of Mattheiss. As they did, we first conclude that, both in Ne and Ar, a HF exchange gives a much larger gap between conduction and valence bands than the experimental one. This result confirms the great influence of correlations in solid rare gases. For Ne, we found a gap of 1.868 Ry (25.41 eV) and for Ar 1.361 Ry (18.52 eV). In both cases, these values are larger than the binding energy of the highest electron in the corresponding free atom. Following the comparison with Lipari and Fowler's results, it can be seen that the order of the levels is the same in both cases, except at point Γ, where we found Γ_{12} lower than Γ'_2.

Rössler, discussing the paper of Lipari and Fowler, questioned their value for the gap. He thought that this gap should be larger since the poor convergence of the upper valence band had not been taken into account. Looking at our value of 18.5 eV, in place of 17.2 eV from Lipari and

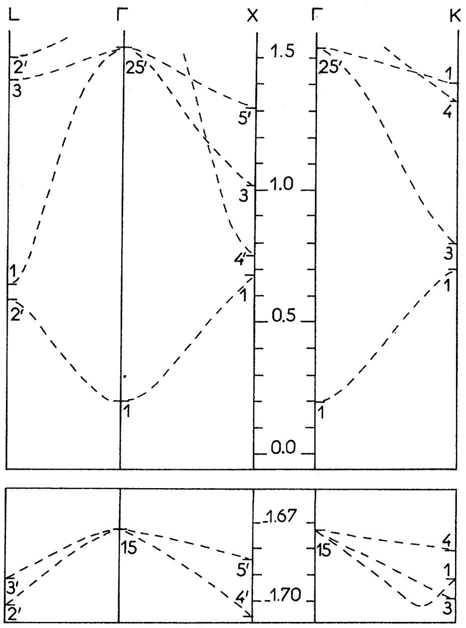

FIG. 1. Neon HF band structure, energies in rydbergs. Note the change in scale between the valence and conduction bands. Calculations were carried out at points Γ, X, L, and K. The connecting lines represent reasonable guesses to the actual shapes of the bands.

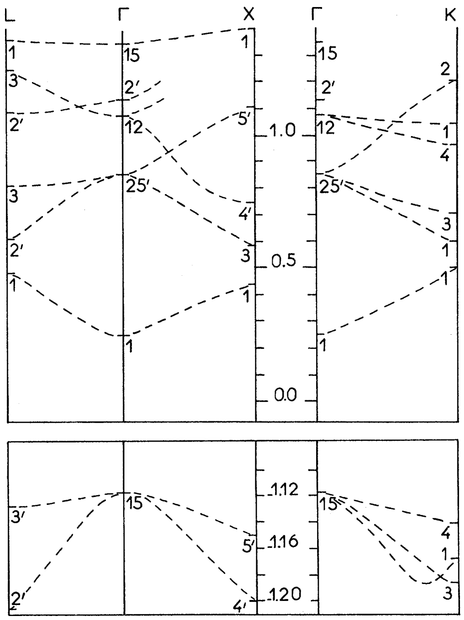

FIG. 2. Argon HF band structure, energies in rydbergs. Note the change in scale between the valence and conduction bands. Calculations were carried out at points Γ, X, L, and K. The connecting lines represent reasonable guesses to the actual shapes of the bands.

Fowler, we agree with this point of view. Such an argument could also explain the discrepancy in the $3p$ bandwidth. We must now remember that we have neglected the contribution of the region outside the APW spheres to exchange. An order of magnitude of this contribution can be obtained by the following calculation. The excited Γ_1 state is approximated, as in the cellular method, by an atomic-like wave function of S symmetry with the right number of modes, which is a solution of the HF equations in the core potential $U(r)$ and has a zero derivative at radius S_B of the Wigner-Seitz sphere. The wave function for the highest valence state is the function $\varphi_{nlm}(\vec{r})$ defined in (1) (with $l=1$, $n=2$ for neon and $n=3$ for argon). From these wave functions, the HF exchange energies $E_X^V(S_A)$ for the valence state and $E_X^C(S_A)$ for the conduction state can be calculated inside a volume restricted to the APW sphere. The corresponding quantities $E_X^V(S_B)$ and $E_X^C(S_B)$ are evaluated inside the Wigner-Seitz cell of radius S_B. The HF exchange contribution to the gap will be $\Delta E_X(S_A)=E_X^C(S_A)-E_X^V(S_A)$ if the exchange is taken into account inside the APW sphere only, and $\Delta E_X(S_B)=E_X^C(S_B)-E_X^V(S_B)$ for the whole cell. The difference $\delta E_X=\Delta E_X(S_B)-\Delta E_X(S_A)$ gives an evaluation of the error made in our treatment of the exchange. We found the following numerical values: $\delta E_X=-0.015$ eV for neon and 0.035 eV for argon. We conclude that the contribution of the region outside the APW sphere to exchange is quite negligible and does not affect our values of the gaps.

Rössler also suggested that the separation of s and d conduction bands given by Lipari and Fowler is too large by several eV. Our results agree with this assumption. For instance, their separation $\Gamma'_{25}-\Gamma_1$ is 10.27 eV, but we find 8.32 eV.

Nevertheless, the conclusion to this section is that the main features of our HF calculation for argon confirm the study of Lipari and Fowler and can be extended to neon.

IV. CORRELATION EFFECTS AND COMPARISON WITH EXPERIMENT

The HF gap $E_G^{\mathrm{HF}}=\Gamma_1-\Gamma_{15}$, as obtained with the method which has been described in previous sections, is compared with the experimental gap E_G^{obs} (Boursey *et al.*[8] for neon, and Batchelder *et al.*[9] for argon). The HF value is too large by 4.0 eV for neon and 4.4 eV for argon.

Fowler has studied the relation between the observed optical spectrum and the corresponding HF energy-band calculation in insulators.[10] We resume and complete this analysis here.

The exact gap is given by the crystal-energy increment when one electron jumps from the highest valence state, where one hole appears, to the lowest conduction state. The exciton levels are not taken into account here. The free-electron wave function extends over the whole crystal and consequently the electron-hole interaction energy is zero. The crystal electrons are polarized in an independent way from the hole and from the free electron; so, the corresponding correlation energies can be added. Let us denote the polarization energy for the electron by Σ_e and the one for the hole by Σ_h. Both are negative. The gap is the sum of the exact energies, which are $\Gamma_1+\Sigma_e$ for the electron and $-\Gamma_{15}+\Sigma_h$ for the hole:

$$E_G=\Gamma_1-\Gamma_{15}+\Sigma_e+\Sigma_h \ . \tag{7}$$

Σ_e and Σ_h have been calculated by Fowler, using the Mott-Littleton approximation.[11] Applying the Franck-Condom principle, the lattice polarization is neglected. The resulting error, $2\Sigma_{\mathrm{FC}}$, on $\Sigma_e+\Sigma_h$ is certainly very small. According to Fowler, one has $-0.2\ \mathrm{eV}\le 2\Sigma_{\mathrm{FC}}\le 0$.

Fowler also neglects the electronic polarization inside the cell where the hole or the free electron is located. This approximation is not justified, and we shall see that the corresponding self-energy $\Delta\Sigma_e+\Delta\Sigma_h$ is of the same order of magnitude as the correction given by Fowler.

The Mott-Littleton classical theory is based on the calculation of Σ_e and Σ_h by an electrostatic potential. The validity of such an approximation has been discussed by Fowler.[10] It is assumed that an electrical charge $\pm e$ is located at the center of a cell and polarizes the atoms in neighboring cells. The energies Σ_e and Σ_h are equal and have the common value Σ_{ML},

$$\Sigma_{\mathrm{ML}}=-e^2(1-1/K_0)(1/2R) \ ,$$

where the value of R depends on the lattice (nearly $\frac{1}{2}a$). K_0 is the optical dielectric constant of the crystal. It was never measured, but was calculated by Fowler[10] from the atomic polarizability, using the Clausius-Mossoti formula. The values obtained by Fowler, as reported in Table IV, are -0.68 eV for neon and -1.10 eV for argon.

The previous polarization correction does not include the electronic correlations between the additional particle (electron or hole) and the electrons in the same cell. Because of the importance of the exchange forces, very different values for the electron and hole can be expected. The contribution $\Delta\Sigma_h$ to the hole self-energy can be estimated with good accuracy by a semiempirical method. A rare-gas solid is bound by van der Waals forces. Wave functions located at different sites do not overlap appreciably; their atomic character is very strong and their modification going from the gas to the solid is slight. The difference between the hole correlation energies in the gas and in the solid is small. $-\Delta\Sigma_h$ is then nearly equal to the

TABLE IV. Correlation corrections to the HF gap and comparison with experiment. (All values expressed in eV.)

	Neon	Argon
E_G^{HF}	25.41	18.52
$2\Sigma_{\mathrm{ML}}$	-1.36^{a}	-2.20^{a}
$\Delta\Sigma_h$	-1.58	-0.32
E_G^{obs}	21.42^{b}	14.16^{c}
$\Delta\Sigma_e$	-1.05	-1.84

[a] Reference 10.
[b] Reference 8.
[c] Reference 9.

correlation energy of the highest electron in the free atom. (The electron energy is defined as the difference between the atom energy and the Ne^+ or Ar^+ ion energy.) Let $\mathcal{E}$ be the HF energy eigenvalue of the least-bound electron in the free atom, and I be the experimental ionization energy. The correlation energy is then $I - |\mathcal{E}|$ and our approximation is

$$\Delta\Sigma_h = I - |\mathcal{E}| \ . \tag{8}$$

The HF ionization energies $|\mathcal{E}|$ are calculated assuming frozen wave functions, and are given by the HF eigenvalues (Koopmans's theorem). We have used a standard nonrelativistic HF computer program. The results are 23.14 eV for the neon $2p$ state and 16.08 for the argon $3p$ state; the corresponding experimental results are 21.56 eV for the neon $2p^{3/2}$ state and 15.76 eV for the $3p^{3/2}$ argon state. The corresponding $\Delta\Sigma_h$ are reported in Table IV. It can be seen that $\Delta\Sigma_h$ is not negligible and must be added to $2\Sigma_{\mathrm{ML}}$, the only contribution which was taken into account by Fowler.

A simple evaluation of $\Delta\Sigma_e$, the correlation energy of the free electron "in the same cell," is not possible. But its value can be obtained as a result of the previous analysis, using the experimental gap value and the formula

$$\Delta\Sigma_e = E_G^{\mathrm{obs}} - E_G^{\mathrm{HF}} - 2\Sigma_{\mathrm{ML}} - \Delta\Sigma_h \ . \tag{9}$$

The $\Delta\Sigma_e$ was found to be -1.05 eV in neon and -1.84 in argon.

These values seem rather large. In fact, the order of magnitude is quite correct. A rough first-principles calculation using the results of Callaway,[12] and a crude scaling law, give very similar numerical results.

$\Delta\Sigma_e$ can be calculated with the help of the polarization potential concept.[12,13] The optical-spectrum properties of the system resulting from the addition of an electron to an atom in its ground state can be explained by an optical potential.[13] For the low energies, this potential can be written as $V_{\mathrm{HF}} + V_p$. V_{HF} is the HF potential and V_p a real and local polarization potential which is slowly varying with the energy. V_p is equal to $-\alpha/2r^4$ (a.u.) when the electron and atom are far away. α is the atomic polarizability. For small values of r, the determination of V_p is very difficult.[12,13]

The polarization potentials of neon and argon have not been computed. Assuming that V_p is known, $\Delta\Sigma_e$ can be calculated by the first-order perturbation formula

$$\Delta\Sigma_e = \int_\Omega |\varphi|^2 V_p \, d\vec{r} \ . \tag{10}$$

A first-principles calculation of the polarization potential has been made by Callaway for the ions Na^+ (isoelectronic with Ne) and K^+ (isoelectronic with Ar). The resulting $\Delta\Sigma_e$ [average value according to formula (10) on the lowest valence state in bcc metallic sodium and potassium] are given in Table II of Ref. 12. Let us assume that in a given isoelectronic sequence, V_p is proportional to the polarizability and that the integral (10) is proportional to the mean electronic density in a cell. [We use here the fact that $|V_p(r)|$ decreases rapidly outside a radius smaller than the cell radius.[12]] We then have the crude scaling law

$$\Delta\Sigma_e(\mathrm{Ne}) = \frac{\alpha(\mathrm{Ne})}{\alpha(\mathrm{Na}^+)} \frac{\Omega(\mathrm{Na})}{\Omega(\mathrm{Ne})} \Delta\Sigma_e(\mathrm{Na}) \tag{11}$$

and a similar formula for argon. Ω is the atomic volume.

According to Callaway the respective values of $\Delta\Sigma_e$ are 0.264 eV (Na) and 0.81 eV (K). The polarizability ratios are, respectively, 2.6 and 1.25. (We use the ionic polarizabilities implied in the asymptotic forms of Callaway's V_p.[12])

The crude formula (11) gives then -1.09 eV for neon (our value given in Table IV is -1.05) and -1.75 eV for argon (-1.84 in Table IV). The agreement is quite satisfactory.

Mittleman has proposed the following formula, corresponding to a statistical approximation:

$$\begin{aligned} V_p &= -\tfrac{1}{2}\alpha/(r^2 + \lambda r_0^2)^2 \ (\mathrm{a.u.}) \ , \\ r_0^2 &= [\tfrac{1}{2}\alpha(1/Z^{1/3})]^{1/2} \ (\mathrm{a.u.}) \ . \end{aligned} \tag{12}$$

λ must be considered as an adjustable parameter; $\lambda = 1$ corresponds to the Thomas-Fermi approximation. The parameter λ could be determined by comparing the diffusion cross section, calculated using V_p, with the experimental one. This work was not done. We used (10) to determine the parameter λ which gives $\Delta\Sigma_e$ the values of Table IV. The following values were found: $\lambda = 1.6$ in neon and 1.7 in argon. This very good agreement suggests that the use of (12) is justified. It would be interesting to see if the study of the diffusion $e^-(\mathrm{Ne})$ and $e^-(\mathrm{Ar})$ leads to the same values of λ.

V. CONCLUSION

For solids with filled and low-lying valence bands, the HF band structure can be calculated in a simple and a nearly exact way, using the APW scheme. The assumption of a negligible contribution of the region outside the APW spheres to exchange has been justified. The method, applied to neon and argon, gives results which are in good agreement with previous calculations of Lipari and Fowler on argon.

The HF gap is larger than the experimental optical gap by several eV, suggesting a very strong influence of the correlations. A satisfactory treatment of these correlations is obtained in a semiempirical manner: The Mott-Littleton approximation gives an evaluation of the interaction of one charge in one cell with all the other cells; the correlation energy for the valence hole is calculated using atomic results. It is shown that a polarization potential is adequate to take into account the correlation energy of the free electron in the same cell.

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Quantum Theory of a Basic Light-Matter Interaction

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Quantum field-theoretical methods are applied to the problem of determining how the exciton-lattice interaction affects the dispersion of an electromagnetic field associated with the exciton-radiation interaction. An exact solution for the retarded Green's function of the radiation field is calculated for a quantum model consisting of three interacting boson fields—photon, exciton, and phonon. The classical Green's function of a damped-harmonic-oscillator model of a dielectric is shown to be a special case of this quantum Green's function. Two sets of dispersion relations are derived; one set has well-defined energy, the other has well-defined momentum. Results of the theory clearly suggest that the exciton-lattice interaction is capable of literally damping out the "polariton" effects associated with the exciton-radiation interaction in the field solutions with well-defined energy. A Poynting theorem based on the classical model is also derived which includes effects of both spatial dispersion and damping.

I. INTRODUCTION

The quantum theory of light-matter interactions in semiconductors and dielectrics has been approached from two different directions. One group[1] has studied the electron-lattice interaction and has shown how it produces damping of excited electronic states (excitons). Another group[2] has studied the electron-radiation interaction and has shown how it produces dispersion of the radiation field. Neither of these groups has dealt rigorously with both the electron-lattice (H_{eL}) and electron-radiation (H_{eR}) interactions simultaneously. These interactions will be given equal attention in the present paper. Quantum-mechanical results are derived which have a form closely resembling results based on a classical damped-harmonic-oscillator model of a dielectric.

A brief discussion of this classical model is given in Sec. II. A generalization of Poynting's theorem is derived which includes effects of both spatial dispersion and damping. From this an energy velocity is defined which determines the speed at which energy (electromagneticlike and/or matterlike) propagates through a classical dielectric.

A quantum field-theoretical model consisting of