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Hartree-Fock Energy Bands for Argon

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The energy bands of Ar are investigated in the Hartree-Fock approximation. We have used localized orbitals self-consistent for the crystal (accurate to first order in the inter-atomic overlap) and the mixed-basis method. The results are compared with previous orthogonalized-plane-wave Hartree-Fock calculations by Lipari and Fowler and augmented-plane-wave calculations by Dagens and Perrot and the agreement is good.

A great deal of effort has been devoted in the past to the calculation of the first-principles energy bands for insulating crystals.¹⁻⁴ The role of electronic correlation has been extensively investigated, together with a better understanding of the limits of the Hartree-Fock approximation. The author,¹ in collaboration with Kunz² and Fowler³ has carried out an extensive investigation of both rare gases^{1,3} and alkali-halide crystals.² The former calculations^{1,3} differ from the latter² in that in the former we used the orthogonalized-plane-wave (OPW) method together with free-atom wave functions and eigenvalues for the core states, whereas in the latter the mixed-basis (MB) method and localized orbitals⁶ were used. Due to these differences, it is hard to compare the two sets of calculations. In particular, it would be interesting to see how much the results will be modified when localized orbitals and the mixed-basis method are used for the rare-gas crystals also. Very recently, Dagens and Perrot⁴ have investigated the Hartree-Fock energy bands of argon, using a

method closely related to the classical augmented-plane-wave (APW) method, which treats in a nearly exact way the Hartree-Fock exchange. Their investigation, while confirming our previous main conclusion,³ finds a smaller separation between the *s* and *d* conduction bands with a slightly larger energy gap. Recently, localized orbitals for Ar have been obtained.⁷ It seems, therefore, very useful to use these orbitals for an investigation of the energy bands of Ar, since such an investigation could answer some of the above questions.

Since the methods of calculation have been described extensively elsewhere,² we will not discuss them here. Very briefly, one first obtains the self-consistent charge density for the crystal, using local orbitals. One then uses the MB method to solve the Hartree-Fock equations.

All the calculations were performed using the Sigma 7 Computer in the Xerox Rochester Technical Computer Center in Webster, New York. The local-orbital core states included in the MB method were the 1*s*, 2*s*, and 2*p* states. In Table I we

TABLE I. The parameters for Ar are given. See Ref. 7 for the definitions of parameters A_{ij} , Z_{ij} , C_{ijk} , and $\epsilon_{i,j}$. $\epsilon_{1s,1s}=237.62$, $\epsilon_{1s,2s}=0.0$, $\epsilon_{2p,2p}=19.145$, $\epsilon_{2s,2s}=24.679$, $\epsilon_{1s,2s}=0.0$, $\epsilon_{3p,3p}=1.1853$, $\epsilon_{3s,3s}=2.5616$, $\epsilon_{2s,3s}=19 \times 10^{-7}$, $\epsilon_{2p,3p}=21 \times 10^{-7}$.

<i>j</i>	A_{0j}	Z_{0j}	A_{1j}	Z_{1j}	C_{10j}	C_{20j}	C_{30j}	C_{21j}	C_{31j}
1	0	20.750	0	16.220	0.876582	0.230465	0.074527	0.026770	0.005201
2	1	14.900	0	8.230	0.444910	0.220711	0.091844	0.900836	0.246130
3	2	16.500	0	5.000	-0.183197	-0.086199	-0.026546	0.388417	0.098199
4	2	10.500	2	8.000	-0.008064	-0.179010	0.000947	0.192066	0.073941
5	1	6.206	1	2.970	0.005543	-0.926627	-0.479853	0.004425	0.814811
6	2	3.166	2	2.211	-0.001087	-0.007752	0.712572	-0.000737	0.399386
7	2	1.993	1	1.370	0.000473	0.000699	0.497281	0.000340	-0.317584

TABLE II. Energy bands for Ar at the points Γ , X , and L of the first Brillouin zone. The notation is that of Ref. 2. Results are shown in eV. The OPW results (Ref. 8) are also given.

Point	Irr. rep.	MB			OPW		
Γ	Γ_1	-34.9448	2.4108	18.2537	-34.8521	2.2544	18.1830
	Γ_{15}	-13.9755	17.1945		-13.9501	17.1273	
	Γ_{25}'	12.2588			12.5555		
	Γ_{12}	15.1121			15.0892		
	Γ_2'	14.3697			14.2872		
X	X_1	-34.4169	5.3034	18.0091	-34.2243	5.2233	18.0727
	X_4'	-16.3660	9.6557		-16.3685	9.6173	
	X_5'	-14.8364	14.3112		-14.8052	14.2987	
	X_3	7.4802			7.4258		
	X_2	18.4729			18.4559		
L	L_1	-34.5538	5.7091	18.2402	-34.3677	5.6461	18.2951
	L_2'	-16.6316	7.6782	13.7742	-16.6544	7.5881	13.7012
	L_3'	-14.4834	18.5701		-14.4544	18.5407	
	L_3	10.7708	17.7128		+10.8956	17.9344	

give the local orbitals and energies.⁷ Argon crystallizes into a fcc structure and has a lattice constant of 5.43 Å.³ We have calculated the energy bands at Γ , X , and L of the first Brillouin zone. At Γ we have included the lowest 13 values of $|\vec{k} + \vec{G}_I|$ (i. e., up to $\langle 440 \rangle$); where \vec{G}_I 's are the reciprocal-lattice vectors. At X and L the calculations have been made including the lowest 22 values of $|\vec{k} + \vec{G}_I|$ (i. e., up to $\langle 522 \rangle$ and $\langle \frac{11}{2}, \frac{1}{2}, \frac{3}{2} \rangle$, respectively). The results are shown in Table II. Also shown for comparison are the corresponding values⁸ obtained using free-atom wave functions and the OPW method. As one can see, there is, in general, a good agreement between the two sets of calculations, thus confirming all the conclusions previously obtained. The separation between the s and d conduction bands ($\Gamma_{25}' - \Gamma_1$) is now 9.85 eV as compared with the previous value of 10.30 eV. This separation is now in better agreement with

the value 8.32 eV obtained by Dagens and Perrot. However, the discrepancy between the two values (9.95 versus 8.32 eV) is still somewhat of a mystery. We suppose that it could be due to the muffin-tin potential approximation used in the APW calculations⁴ since such discrepancies exist also between our calculation and those of Rössler,⁹ who also made use of the muffin-tin approximation. The present value for the energy gap ($\Gamma_1 - \Gamma_{15}$) is 0.2 eV larger than the one obtained using the OPW method, and free-atom wave functions. This is also consistent with the larger energy-gap value obtained by Dagens and Perrot. The rest of the bands change very little in going from the OPW to the MB calculation. Therefore all the main conclusions obtained in Ref. 3 are valid, in particular those on the importance of including correlation effects before comparison with experiment is attempted.

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