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Proposed $X_{\alpha\beta}$ Method for Solids*

A. M. Boring
University of California, Los Alamos Scientific Laboratory, Los Alamos, New Mexico 87544

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Results of atomic calculations pertinent to the use of Herman's $X_{\alpha\beta}$ method in energy-band calculations are given. With α fixed at $\frac{2}{3}$, two β parameters were determined for each atom, one satisfying the virial theorem, and the other the variational principle. The object of these calculations was to determine the sensitivity of β to changes in charge-density inhomogeneity in going from one atom to the next and the sensitivity to the potential shift of a given atom obtained by turning on the Latter potential. These results are compared with those of Kmetko on the X_α method. The results reported here indicate that a β of 0.0040 should be used in applying the $X_{\alpha\beta}$ method in solids.

In this paper the results of a study of the sensitivity of Herman's $X_{\alpha\beta}$ local-exchange potential[1] to the Latter potential and the inhomogeneous charge density in atomic systems are reported. Slater has suggested[2] a method, based on the determination of the α parameter in the free atom, for using the X_α local-exchange potential in a crystal. In a crystal one can only determine the energy by the statistical method, so the variational principle and the virial theorem are not available to aid in the determination of α. For this reason Slater has proposed that one use X_α orbitals for the atom and determine both the α that satisfies the virial theorem and the different α that minimizes the total energy of the atom as calculated via Hartree-Fock theory. Slater has indicated that the α that satisfies the virial theorem would be the more appropriate one to use in the crystal.

Kmetko[3] has obtained the set of α's that minimize the total energy for all atoms in the Periodic Table. He obtained results both with and without the Latter potential. Since Kohn and Sham[4] have shown that for a nearly homogeneous electron gas the variational principle requires $\alpha = \frac{2}{3}$ for the one-electron eigenvalue equations, deviations from this value can be taken as an indication of the inhomogeneity of the system.

In Herman's $X_{\alpha\beta}$ method this inhomogeneity is accounted for by including gradient corrections in the local exchange. The local-exchange operator is then written as

$$V_X^{\alpha\beta}(r) = [\alpha + \beta G(r)]\, V_{XS}(r), \tag{1}$$

where

$$G(r) = \frac{1}{\rho^{2/3}(r)} \left[\frac{4}{3} \left(\frac{\nabla\rho(r)}{\rho(r)} \right)^2 - 2\, \frac{\nabla^2\rho(r)}{\rho(r)} \right]$$

and

$$V_{XS}(r) = -6 \left(\frac{3\pi}{8}\, \rho(r) \right)^{1/3} ,$$

and $\rho(r)$ is the self-consistent charge density.

Herman has shown the oscillating structure of $G(r)$ for the krypton atom,[5] and this structure was found to be typical of all the atoms studied.

Since the main goal of this study was to determine the sensitivity of β, α was set to the homogeneous-electron-gas value of $\frac{2}{3}$. The β that satisfied the virial theorem (β_ν) and the β that minimized the total energy ($\beta_{\min}$) when calculated via Hartree-Fock theory were then determined. In order to make a general study, but without studying

TABLE I. The set (β_ν, $\beta_{\min}$) for selected atoms.

		Latter		No Latter	
Atom	Z	β_ν	$\beta_{\min}$	β_ν	$\beta_{\min}$
Ne	10	0.0060	0.0072	0.0036	0.0052
K	19	0.0042	0.0042	0.0040	0.0022
Mn	25	0.0040	0.0044	0.0038	0.0048
Cu	29	0.0040	0.0058	0.0036	0.0066
As	33	0.0042	0.0060	0.0040	0.0058
Tc	43	0.0042	0.0048	0.0040	0.0054
Sb	51	0.0042	0.0052	0.0040	0.0052
Eu	63	0.0040	0.0048	0.0038	0.0038

TABLE III. Total energies (in Ry).

	Latter		No Latter	
	$E_{\alpha\beta}$	E_α [a]	$E_{\alpha\beta}$	$E_{\rm HF}$ [b]
Ne	− 257.023	− 257.067	− 257.082	− 257.094
K	− 1 198.312	− 1 198.189	− 1 198.315	− 1 198.330
Mn	− 2 299.187	− 2 299.175	− 2 299.205	− 2 299.252
Cu	− 3 277.786	− 3 277.814	− 3 277.847	− 3 277.928
As	− 4 468.273	− 4 468.258	− 4 468.307	− 4 468.345
Tc	− 8 409.151	− 8 409.118	− 8 409.170	− 8 409.215
Sb	− 12 626.779	− 12 626.750	− 12 626.813	− 12 626.85
Eu	− 20 846.032	− 20 846.000	− 20 846.043	− 20 846.16

[a] Calculated in the present study.

[b] Obtained from Mann's nonrelativistic Hartree-Fock program Los Alamos Report No. LA-3690, 1967 (unpublished).

all the atoms in the Periodic Table, a series of eight atoms was chosen in which the valence orbitals all have different (n, l) character. These are Ne($2p^6$), K($4s$), Mn($3d^5 4s^2$), Cu($3d^{10} 4s^2$), As($4s^2 4p^3$), Tc($4d^5 5s^2$), Sb($5s^2 5p^3$), and Eu($4f^7 6s^2$). The study was not carried beyond Eu because the calculations are nonrelativistic. The set (β_ν, $\beta_{\min}$) was determined for these atoms both with and without the Latter potential $[V(r) \sim -1/r$ at large $r]$, and the results are shown in Table I. $\beta_{\min}$ is seen to vary considerably, but β_ν (except for Ne) is quite insensitive both to charge density inhomogeneity and to Latter potential. In Table II the changes determined in β and in α, due to the shift in atomic potential as the Latter potential is turned on, are given. Here

$$\Delta\beta = \beta(\text{Latter}) - \beta(\text{no Latter}),$$

$$\Delta\alpha = \alpha(\text{Latter}) - \alpha(\text{no Latter}).$$

It is seen that $\beta_\nu = 0.0040 \pm 0004$ (except for Ne). This shift in the potential of the isolated atom is not the same as the shift in the potential in going from an isolated atom to a solid, but the electronic states that change most drastically when atoms form a solid are the ones most affected by this kind of potential shift and in this sense this result indicates that β_ν should not change in going to the solid. In Table III the total energies are given, and one can see that $E_{\alpha\beta}$ with no Latter correction (energy calculated by Hartree-Fock theory with $X_{\alpha\beta}$ orbitals) is much closer to the Hartree-Fock value ($E_{\rm HF}$) than is E_α (energy calculated by Hartree-Fock theory with X_α orbitals).

In an attempt to find some relationship between the X_α and $X_{\alpha\beta}$ methods, several averages of $\langle \frac{2}{3} + \beta G(r) \rangle$ were taken. The objective was to determine whether some average of $\langle \frac{2}{3} + \beta G(r) \rangle$ was equal to the $\alpha_{\min}$ that minimizes the total energy in the X_α method. The averages chosen were

$$\alpha_{\rm I} = \tfrac{2}{3} + \beta \int_0^\infty G(r) dr,$$

$$\alpha_{\rm II} = \tfrac{2}{3} + \beta \int_0^\infty G(r)\rho(r) dr \Big/ \int_0^\infty \rho(r) dr,$$

$$\alpha_{\rm III} = \tfrac{2}{3} + \beta \int_0^\infty G(r)\rho(r)^{1/3} dr \Big/ \int_0^\infty \rho(r)^{1/3} dr,$$

$$\alpha_{\rm IV} = \tfrac{2}{3} + \beta \int_0^\infty G(r)\rho(r)^{4/3} dr \Big/ \int_0^\infty \rho(r)^{4/3} dr .$$

In Table IV the values obtained for the atoms studied are shown. The average in which $G(r)$ is weighted by $\rho(r)^{1/3}$ was taken because this is the effective weighting in the one-electron-eigenvalue equation. The effective weighting of the exchange contribution to the total energy is $\rho^{4/3}(r)$. As can be seen from Table IV the differences between

TABLE II. Differences in β_ν, $\beta_{\min}$, and $\alpha_{\min}$ due to Latter potential correction.

Atom	$\Delta\beta_\nu$	$\Delta\beta_{\min}$	$\Delta\alpha_{\min}$ [a]	$\alpha_{\min}$ [a]
Ne	0.0024	0.0020	0.077	0.741
K	0.0002	0.0020	0.011	0.709
Mn	0.0002	0.0004	0.019	0.714
Cu	0.0004	0.0008	0.026	0.733
As	0.0002	0.0002	0.016	0.711
Tc	0.0002	0.0016	0.016	0.701
Sb	0.0002	0.0000	0.018	0.689
Eu	0.0002	0.0010	0.009	0.695

[a] Obtained from Ref. 3.

TABLE IV. Averages of $\langle \frac{2}{3} + \beta G(r) \rangle$.

Atom	$\alpha_{\rm I}$	$\alpha_{\rm II}$	$\alpha_{\rm III}$	$\alpha_{\rm IV}$	Δ_1 [a]	Δ_2 [b]
Ne	0.537	0.699	0.662	0.750	0.009	0.074
K	0.399	0.673	0.655	0.690	0.019	0.042
Mn	0.549	0.679	0.662	0.706	0.008	0.047
Cu	0.400	0.679	0.644	0.713	0.020	0.066
As	0.440	0.679	0.655	0.705	0.006	0.044
Tc	0.482	0.675	0.656	0.696	0.005	0.034
Sb	0.386	0.674	0.652	0.693	0.004	0.022
Eu	0.500	0.671	0.659	0.684	0.011	0.028

[a] $\Delta_1 = |\alpha_{\rm IV} - \alpha_{\min}|$.

[b] $\Delta_2 = |\frac{2}{3} - \alpha_{\min}|$.

α_{min}'s and α_{IV}'s is small. Although $G(r)$ oscillates and samples each orbital differently its effect in the calculation of the total exchange energy is very similar to that of α_{min}. This comparison between the factors multiplying the $\rho^{1/3}(r)$ exchange is possible because the charge densities determined from the $X_{\alpha\beta}$ and X_α method do not differ significantly. The calculated $G(r)$ was modified at large and small values of r in the same manner as in Herman's work.[1]

The results of many energy-band calculations have been shown to be sensitive to the exchange potential, and Slater's scheme, which is guided by first-principles arguments, seems more appealing than empirically determining α (or β) in a solid. However, the energy-band calculation of Cu by Snow[6] seems to indicate that the $\alpha = 0.83$ results are in much better agreement with experimental results from photoemission data, magnetoacoustic studies, and de Haas–van Alphen work than is $\alpha = 0.67$. Since $\alpha = 0.721$ is the value one would use in Slater's scheme, it is not clear that it will give the best results in some crystals. An energy-band study of Cu based on Herman's $X_{\alpha\beta}$ scheme, with $\beta = 0.0040$, is being undertaken to determine its merits.

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Open-Orbit Resonances and Magnetic Field Dependence of the Ultrasonic Attenuation of Shear Waves in Magnesium†

R. V. Kollarits and J. Trivisonno
Physics Department, John Carroll University, Cleveland, Ohio 44118

and

R. W. Stark
The James Franck Institute and the Department of Physics, University of Chicago, Chicago, Illinois

(Received 20 February 1970)

The open-orbit resonances in the ultrasonic attenuation of shear waves in magnesium have been studied. The ultrasonic open-orbit resonances have been observed for magnetic fields applied in the basal plane for fields as high as 1100 G. The existence of the open-orbit resonance provides direct evidence for the presence of a spin-orbit–induced energy gap in the *AHL* Brillouin-zone plane. The period of the open orbit is in excellent agreement with the Brillouin-zone dimension in the [0001] direction. The effects of magnetic breakdown are observed to be of importance in fields of about 1 kG.

INTRODUCTION

Recent magnetoacoustic attenuation[1] and de Haas–van Alphen[2] experiments have led to a quantitatively accurate understanding of the electronic band structure[3] of magnesium. The nonlocal-band-structure calculation reported in Ref. 3 provided for the experimental data a detailed description whose accuracy was limited only by a calculational truncation error of about 1.5×10^{-3} Ry. This, however, was not sufficient to provide any information about the magnitude of spin-orbit splitting energy gaps which Cohen and Falicov[4] and Falicov and Cohen[5] had previously estimated to be about 5×10^{-4} Ry. As a consequence, the effects of spin-orbit coupling were included in Ref. 3 only through the implicit use of the single-zone scheme as a basis for the description of the