fective spin-spin interaction parameter ρ is less easy to compare since there are quite a few contributing mechanisms: (i) the actual spin-spin interaction estimated by Watson and Blume to be $\rho_0 = 0.18\ \text{cm}^{-1}$ for Fe^{2+}.[12] (ii) Second-order spin-orbit coupling with the higher electronic levels of the $3d^6$ ion: In free Fe^{2+} Pryce[13] estimates $0.95\ \text{cm}^{-1}$ for the sum of effects (i) and (ii), so that this would be $0.77\ \text{cm}^{-1}$ for the latter. However, it is not known how much these levels and their spin-orbit-coupling constants change in the crystal. (iii) The third-order spin-orbit interaction between the ^5E and the $^5T_2$ states gives an effect of about the same magnitude as (i) but with the opposite sign.

The present work shows that the Mössbauer spectra of Fe^{2+} at tetrahedral cubic sites, as in $Fe_{0.02}Cd_{0.98}Cr_2S_4$, can very satisfactorily be described on the basis of the simple model incorporating a crystal field, an exchange field, and a second-order spin-orbit coupling. The serious deviations from this picture, as observed in $FeCr_2S_4$,[3] are absent in the dilute system.

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Optimization of the Statistical Exchange Parameter α for the Free Atoms H through Nb[†]

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We have examined two criteria for determining the exchange parameter α which occurs in the $X\alpha$ local-statistical-exchange approximation, an approximation widely used in energy-band and molecular calculations. These criteria are (i) adjustment of the statistical total energy to the Hartree-Fock total energy, leading to α_{HF}, and (ii) satisfaction of the virial theorem, leading to α_{vt}. We have calculated the values of the parameter α corresponding to these two criteria for the neutral atoms H through Nb, and compared them with the values α_{min} corresponding to the Hartree-Fock total-energy minimization criterion employed earlier by Kmetko and Wood. While the last-mentioned criterion leads to α values which show large fluctuations across the periodic table as a function of Z, the α values obtained by either of the two criteria used in this paper show a systematic variation as a function of Z, reflecting the shell structure of the atoms, and varying linearly with Z within the range of Z for which a particular atomic subshell is being filled.

Slater and Johnson[1] have proposed a so-called self-consistent-field (SCF) $X\alpha$ method for handling polyatomic molecules and solids, based on the statistical approximation for treating exchange in form of the $X\alpha$ method. In Sec. IV of that paper they have suggested a criterion for determining a value of the parameter α. The present paper outlines calculations which have been made to obtain the α values for free atoms with atomic numbers up to 41. The suggested scheme was to determine the parameter α in an atomic calculation and use the same values in molecular or solid-state calculations. The proposed criterion for determining the exchange parameter in an atom was to choose

TABLE I. Exchange parameters α_{vt} and α_{HF} and derivatives of statistical energy with respect to α given for atoms in their ground state.

	α_{vt}	α_{HF}	$\frac{\partial\langle E_{X\alpha}\rangle}{\partial\alpha}$		α_{vt}	α_{HF}	$\frac{\partial\langle E_{X\alpha}\rangle}{\partial\alpha}$
H	0.97804[a]			Ti	0.71648	0.71695	−114.8
He	0.77236	0.77298	−2.6	V	0.71506	0.71556	−123.3
Li	0.78087	0.78147	−4.5	Cr	0.71296	0.71352	−133.2
Be	0.76756	0.76823	−6.9	Mn	0.71228	0.71279	−142.1
B	0.76452	0.76531	−9.8	Fe	0.71094	0.71151	−153.1
C	0.75847	0.75928	−13.2	Co	0.70966	0.71018	−162.7
N	0.75118	0.75197	−17.2	Ni	0.70843	0.70896	−173.6
O	0.74367	0.74447	−21.8	Cu	0.70635	0.70697	−186.2
F	0.73651	0.73732	−27.1	Zn	0.70619	0.70673	−197.3
Ne	0.72997	0.73081	−33.1	Ga	0.70644	0.70690	−208.3
Na	0.73044	0.73115	−38.4	Ge	0.70645	0.70684	−219.0
Mg	0.72850	0.72913	−43.9	As	0.70630	0.70665	−230.9
Al	0.72795	0.72853	−49.6	Se	0.70606	0.70638	−242.0
Si	0.72696	0.72751	−55.7	Br	0.70576	0.70606	−253.9
P	0.72569	0.72620	−62.2	Kr	0.70544	0.70574	−266.8
S	0.72426	0.72475	−69.0	Rb	0.70525	0.70553	−278.4
Cl	0.72277	0.72325	−76.2	Sr	0.70480	0.70504	−290.1
A	0.72131	0.72177	−83.7	Y	0.70440	0.70465	−301.5
K	0.72072	0.72117	−90.7	Zr	0.70398	0.70424	−313.7
Ca	0.71941	0.71984	−98.0	Nb	0.70357	0.70383	−327.0
Sc	0.71793	0.71841	−105.9				

[a] See Ref. 3.

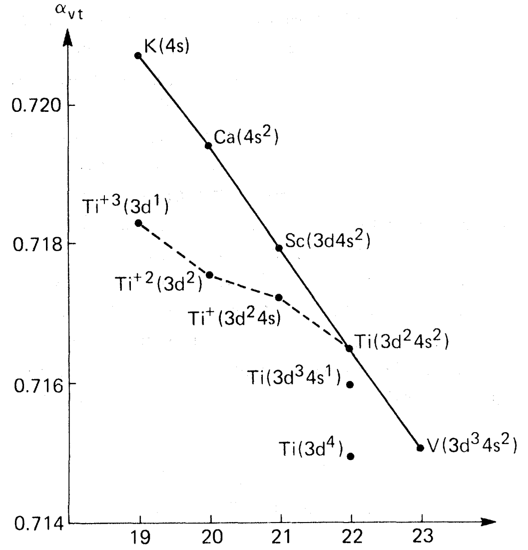

FIG. 2. α_{vt} values of Ti for different ionicities and configurations are compared with the α_{vt} values of the corresponding neutral atoms with the same number of electrons.

α so that the statistical total energy $\langle E_{X\alpha}\rangle$ defined in Eqs. (2) and (3) of Ref. 1 should equal the configuration-averaged Hartree-Fock (HF) energy $\langle E_{HF}\rangle$, as determined by Mann.[2] We shall denote the resulting value of α by α_{HF}. Values of α_{HF} for the lighter elements are tabulated in Table I and shown in Fig. 1. A modified Herman-Skillman[4] program was used to carry out the $X\alpha$ self-consistent calculations. To evaluate the necessary integrals for the total energy, Zare's integral program[5] was incorporated. The calculations were performed on an IBM 360/65 using double-precision arithmetic. Latter's[6] tail correction was not used.

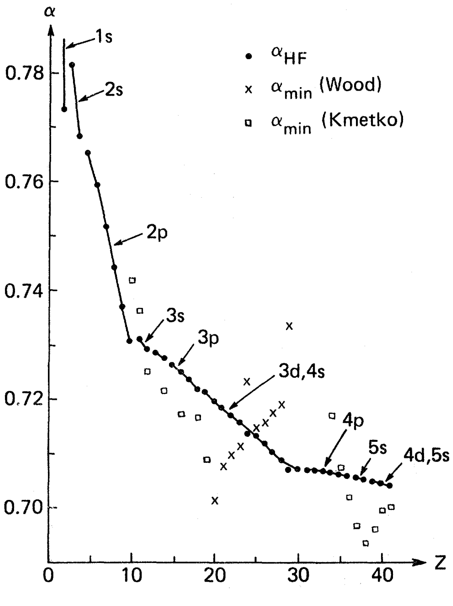

FIG. 1. Exchange parameter α calculated in different ways vs atomic number Z.

As we see from Fig. 1, the values of α_{HF} within a given shell vary almost linearly with Z, always decreasing. That Cr (ground-state configuration $3d^5 4s$) and Cu ($3d^{10}4s$) deviate slightly from the straight line may be due to the fact that these are the only atoms in this series with only one $4s$ electron. On the other hand, Kmetko[7] and Wood[8] obtained the exchange parameter α by minimizing a total energy which we may symbolize by $\langle E_{HF}(\alpha)\rangle$ as a function of α. This quantity $\langle E_{HF}(\alpha)\rangle$ is computed using the formula for the HF total energy, but the $X\alpha$ orbitals. This is the method suggested by Lindgren.[9] We denote this value of α by α_{min}. The resulting values α_{min} are also shown in Fig. 1. They show an over-all decrease in magnitude with increasing Z, as for α_{HF}, but with superposed irregularities. Since the minimum of $\langle E_{HF}(\alpha)\rangle$ vs α for each atom is very flat, the use of α_{HF} instead of α_{min} results in a practically negligible increase of $\langle E_{HF}(\alpha)\rangle$ as compared with the use of α_{min}.

The calculation of α_{HF} can be carried out for configurations for which Mann's calculations have been made. For other cases, it is more convenient to have a method of calculation using only the $X\alpha$ computer programs, without the need of also using the HF programs. Such a method is based on the suggestion of Berrondo and Goscinski[10] and others[11,12] that one choose α so that if we compute the kinetic and potential energies using the HF formulas but the $X\alpha$ orbitals, which we can denote as $\langle T_{HF}(\alpha)\rangle$

and $\langle V_{HF}(\alpha)\rangle$, respectively, the virial theorem $\langle V_{HF}(\alpha)\rangle = -2\langle T_{HF}(\alpha)\rangle$ is satisfied. We call this value α_{vt}, and tabulate it as well as α_{HF} in Table I. The close agreement between α_{vt} and α_{HF} is clear from this tabulation. We also give in Table I the value of $\partial\langle E_{X\alpha}\rangle/\partial\alpha$. This is of convenience to workers who wish to take advantage of the practically linear nature of $\langle E_{X\alpha}\rangle$ as a function of α. The linear curves obtainable from Table I are of sufficient accuracy so that deviations from them in the range $\frac{2}{3} < \alpha < 1$ are negligible. For example, in a band-structure calculation of NbN these derivatives have been used to calculate an average value of the exchange parameter for the compound solid.[13]

In Fig. 2 we give values of α_{vt} determined for the Ti atom in several ionizations and configurations as compared with the α_{vt} values of the corresponding neutral atoms of the same number of electrons. The corresponding results for α_{HF} would be very similar, but more difficult to compute. The reason for carrying out this calculation was that the statistical-exchange correlation is important for applications to solids and molecules. Since the ionicity and configuration is often uncertain in these cases, and is likely to vary from compound to compound, it is important to find how much effect the change of ionicity or configuration will have on α. The results of Fig. 2 show that α_{vt} does not change much for different ionicities or configurations, and it is to be assumed that the same results will also hold for α_{HF}. Therefore it seems justified to determine the parameter α_{HF} for the atom and use it for calculation in a solid or molecule.

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