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Accurate calculation of spin-orbit coupling constants for 3*d* atoms and ions with effective core potentials and reduced basis sets

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We present an approximate method for obtaining spin-orbit coupling constants of 3*d* atoms and ions from an effective one-body Hamiltonian. The method, suggested by numerical results of the analytical theory of Blume and Watson [Proc. R. Soc. London, Sect. A **270**, 127 (1962); **271**, 565 (1963)], incorporates the model potential approach of Bonifacic and Huzinaga [J. Chem. Phys. **60**, 167 (1974)] for representing the core-valence interactions. In combination with reduced valence basis set, the new procedure gives accurate spin-orbit constants for the 3*d* atoms, and slightly less accurate values for di- and tripositive 3*d* ions. These results suggest that this method can be an accurate economic route to crystal calculations of the spin-orbit constants within any cluster-model approach involving the Hamiltonian of Misetich and Buch [J. Chem. Phys. **41**, 2524 (1964)].

INTRODUCTION

The theoretical calculation of the optical spectrum of transition-metal ions in crystals generally requires adequate consideration of the spin-orbit coupling. This interaction is the main contributor to the splitting of the crystal multiplets and can mix electronic states of different spin multiplicity. This mixing may be an important factor in the study of the intensity pattern of the spectrum.

Misetich and Buch[1] have shown that the crystal spin-orbit Hamiltonian can be approximated, within the cluster model, by a sum of effective one-body interactions running over the transition-metal ion and the neighbor atoms. This useful approximation transforms the cluster calculation of the spin-orbit constant into a series of atomic-type calculations. Clearly, the cluster electron density is needed for obtaining these atomic-type spin-orbit constants since the electron relocalization due to the metal-ligand bonding modifies their free-ion values.

We will not discuss here this type of modification. Rather, we will consider the current theory of the atomic spin-orbit constants and will present and discuss an approximate procedure for obtaining these quantities. This procedure makes use of three approximations often incorporated in crystal calculations: a one-body spin-orbit Hamiltonian, effective core potentials for dealing with the core-valence interactions, and small-size valence basis sets. The aim of this paper is to show that the atomic-type spin-orbit constants of the 3*d* atoms and ions computed within these approximations are very close to the analytical values deduced from the exact theory and large basis sets. The interest of this result in the calculation of the spin-orbit constant of 3*d* ions in crystals is apparent.

The theory of the atomic spin-orbit coupling in many-electron atoms has been discussed many times in the literature. The simplest description of this interaction has been done by extension of the one-electron operator deduced from the reduction of the Dirac equation to nonrelativistic form.[2] The usually called "complete" spin-orbit interaction[3] comes from the derivation by Bethe and Salpeter,[4] and by Slater,[5] of a spin-orbit Hamiltonian which includes one- and two-body interactions. Starting from this Hamiltonian and following the work of Elliot[6] and Horie,[7] Blume and Watson developed a theory of the spin-orbit constants,[8] and performed calculations for 2*p*, 3*p*, 3*d*, and 4*p* atoms and ions using Hartree-Fock functions.[9] Froese-Fischer[10] and Malli[11] reported complete spin-orbit calculations for a number of cases, but the most extensive calculations have been carried out by Fraga and co-workers.[3,12–16]

These calculations have been done with high-quality Hartree-Fock-Roothaan functions or numerical Hartree-Fock functions.[16] This level of quality is hardly transferable to crystal calculations, where some approximations are generally mandatory. See, for example, the recent complete neglect of differential overlap calculation of the spin-orbit constant of Cu^{2+} in ZnS and CdS by Setyono and Scherz.[17]

In this work we present an approximate method for computing accurately the atomic spin-orbit constant without using large basis sets. The method is aimed to be a useful scheme for crystal calculations within the cluster model, in the context of Misetich and Buch's approximation.[1]

The idea of the method is simple: the study of the numerical results of analytical calculations performed with large basis sets suggests that an effective one-body spin-orbit Hamiltonian could give sufficiently accurate values for the complete spin-orbit constants. The effective central potential required for such a calculation can be approximated, for instance, by following Huzinaga's model potential approach.[18] In line with this scheme, the valence basis set could be noticeably reduced. This reduction would make the method particularly adequate for those cluster calculations involving small valence bases and active self-consistent-field spaces limited to the valence shell.

In the following section we give the details of the proposed scheme, with particular reference to the theory of Blume and Watson.[8] In the last section we report numerical results for the $3d$ atoms and ions. These results show that this scheme is an excellent approximation to the standard achieved when the analytical theory is used in combination with high-quality basis sets. The reasons for this agreement, related to a compensation of the errors introduced by the effective potential approximation and the use of reduced basis sets, are clarified and discussed.

THEORETICAL CONSIDERATIONS

The spin-orbit Hamiltonian for the N-electron atoms can be written, in Hartree units, in the form[8]

$$H_{\text{s.o.}}=\tfrac{1}{2}\alpha^2 Z\sum_{i}^{N} r_i^{-3}\mathbf{l}_i\cdot\mathbf{s}_i-\tfrac{1}{2}\alpha^2\sum_{\substack{i,j\\(i\neq j)}}^{N} r_{ij}^{-3}(\mathbf{r}_{ij}\times\mathbf{p}_i)\cdot(\mathbf{s}_i+2\mathbf{s}_j)\;, \tag{1}$$

where α is the fine-structure constant.

Following the work of Elliot,[6] Blume and Watson simplify Eq. (1) by considering atoms with a single open shell outside a number of closed shells (the core). In the $3d$ systems discussed here, the valence $4s$ atomic orbital (AO) will be either empty or doubly occupied, the only open shell being the $3d$ AO. The core will be made of the $1s$, $2s$, $2p$, $3s$, and $3p$ AO's. Recalling that (a) the sum over closed shell vanishes for the first term in Eq. (1) and (b) the core-valence contributions from the second term can be represented in the form $\sum_i \mathbf{l}_i\cdot\mathbf{s}_i$, Eq. (1) becomes

$$H_{\text{s.o.}}=\zeta_c\sum_i{}'\mathbf{l}_i\cdot\mathbf{s}_i-\tfrac{1}{2}\alpha^2\sum_{\substack{i,j\\(i\neq j)}}{}' r_{ij}^{-3}(\mathbf{r}_{ij}\times\mathbf{p}_i)\cdot(\mathbf{s}_i+2\mathbf{s}_j)\;, \tag{2}$$

where the prime on the summations indicates that only open-shell electrons are to be included.

Furthermore, Horie showed that a part of the open-shell–open-shell two-body interactions [the second term in Eq. (2)] behaves like an effective one-body spin-orbit term.[7] Using this result, Blume and Watson rearrange the spin-orbit Hamiltonian in the form

$$H_{\text{s.o.}}=\zeta'\sum_i{}'\mathbf{l}_i\cdot\mathbf{s}_i-\left[\tfrac{1}{2}\alpha^2\sum_{\substack{i,j\\(i\neq j)}}{}' r_{ij}^{-3}(\mathbf{r}_{ij}\times\mathbf{p}_i)\cdot(\mathbf{s}_i+2\mathbf{s}_j)+(\zeta'-\zeta_c)\sum_i{}'\mathbf{l}_i\cdot\mathbf{s}_i\right]\;, \tag{3}$$

where ζ' is chosen so that the term in large parentheses is not representable, within a given configuration, in the form $\sum_i \mathbf{l}_i\cdot\mathbf{s}_i$. This term is usually known as the residual "spin-other-orbit" interaction.

The spin-own-orbit constant ζ_c in Eq. (2) contains the effects of the bare nucleus plus the shielding of the nuclear charge produced by the closed-shell–open-shell interactions. The antisymmetry of the N-electron wave function gives rise to direct- and exchange-type terms in the calculation of ζ_c. Blume and Watson gave expressions for ζ_c in terms of spin-orbit radial integrals.[8] Here it will be convenient to distinguish the core-$3d$ contribution, ζ_c^0, and the $4s$-$3d$ contribution, ζ_c^*, namely,

$$\zeta_c=\zeta_c^0+\zeta_c^*\;. \tag{4}$$

Moreover, the constant ζ' in Eq. (3) differs from ζ_c by the two-body open-shell–open-shell contributions representable as a one-body coupling. Expressions for ζ' were also given by Blume and Watson in the form[8]

$$\zeta'=\zeta_c^0+\zeta_c^*+\sum_k a_k M^k\;, \tag{5}$$

where the M^k radial integrals were defined by Marvin.[19]

Both ζ_c and ζ' are rigorously constant within a given configuration if the radial functions of the different multiplets are the same.[8] However, the complete spin-orbit constant, which includes the residual spin-other-orbit interaction discussed by Horie,[7] does not have this property. For $3d$ systems it can be written in the form[3]

$$\zeta(d^n;SL)=\zeta_c^0+\zeta_c^*+\sum_k a_k M^k+\sum_k b_k M^k=\zeta_c^0+\zeta^*\;, \tag{6}$$

where the b_k's depend on the multiplet and can be determined from Horie's formulas[7] or from Ref. 3. In Eq. (6), ζ^* contains all the valence-valence spin-orbit interactions.

Using Watson's analytical Hartree-Fock wave functions, Blume and Watson computed the spin-orbit constants for many $2p$, $3p$, $3d$, and $4p$ ions.[9] For the $3d$ ions considered here they found the following:[9]

(a) The computed values of ζ' are in good agreement with available experimental data.

(b) Both direct- and exchange-type terms in ζ_c are important, the latter being about 25% of the former. These terms shield the nuclear charge and then reduce the nuclear spin-orbit constant.

(c) The $3d$-$4s$ and $3d$-$3d$ contributions to the spin-orbit constant, including the residual spin-other-orbit interaction, are small.

The basic idea of the present work emerges from these conclusions. According to them, the spin-orbit constants of the $3d$ systems might be computed with reasonable accuracy by means of an effective one-body spin-orbit operator, i.e.,

$$H_{\text{s.o.}}=\zeta_{\text{eff}}\sum_i \mathbf{l}_i\cdot\mathbf{s}_i\;, \tag{7}$$

with

$$\begin{aligned}\zeta_{\text{eff}}&=\tfrac{1}{2}\alpha^2\langle 3d\,|\,r^{-1}\partial V_{\text{eff}}(r)/\partial r\,|\,3d\rangle+\zeta^*\\&=\zeta_{\text{eff}}^0+\zeta^*\;,\end{aligned} \tag{8}$$

where $V_{\text{eff}}(r)$ is an effective central potential containing the effects of the nucleus and the core electrons. Notice that ζ^* in the above equation is the $3d$-valence spin-orbit constant introduced in Eq. (6).

Clearly, the effective spin-orbit constant ζ_{eff} will not be constant within a given configuration since it is a simulation of the complete spin-orbit constant $\zeta(d^n;SL)$. The question is to know how good this simulation could be.

The use of ζ_{eff} as an approximation to $\zeta(d^n;SL)$ introduces two types of errors, one due to the effective potential approach, and another one associated with the use of a small basis set. Both errors affect the constant ζ^0_{eff} but only the latter has influence on ζ^*. The separate effects of these two errors are examined numerically below.

The remaining question is to determine $V_{\text{eff}}(r)$. In Hartree-Fock theory the potential energy of a valence electron in the field of the nucleus, of charge Z, and the core electrons is[5]

$$V(\mathbf{r}) = -Z/r + \sum_c (2J_c - K_c) , \tag{9}$$

where J_c and K_c are the Coulomb and exchange core operators, respectively. Due to the nonlocal character of K_c, the meaning of the radial derivative $\partial K_c/\partial r$ appearing in Eq. (8) must be defined.[8] We can avoid this difficulty if the core-valence interactions are approximated by an effective core potential. We have considered here the model potential approach of Bonifacic and Huzinaga.[18] According to this method, the core-valence interactions can be very well approximated by means of a (local) radial operator, the model potential, of the form

$$V_{\text{eff}}(r) = -[(Z-N_c)/r] \times \left[1 + \sum_k^{\mathcal{N}} A(k) r^{n(k)} \exp[-\alpha(k) r] \right] , \tag{10}$$

where N_c is the number of core electrons and $\mathcal{N}$, $n(k)$, $A(k)$, and $\alpha(k)$ are parameters to be optimized. Bonifacic and Huzinaga[18] select the values of these parameters by minimizing the difference in shape and energy between the reference all electron orbitals and the approximate valence orbitals.

We have recently obtained exponential model potentials appropriate for the $3d$ atoms and ions by using Huzinaga's techniques.[20] In that calculation[20] we used Clementi and Roetti's 2ζ basis sets[21] as reference since these bases are, in general, sufficiently accurate for most applications. However, here we want to compare the model potential approach with the exact calculation of Blume and Watson. Accordingly, we have prepared new model potentials by using as a reference set the high-quality, multi-ζ bases of Clementi and Roetti.[21] The parameters of these new potentials have been obtained by means of a simple and efficient procedure. First, following the ideas of Katsuki and Inokuchi,[22] the analytical potential in Eq. (9), computed with the high-quality basis set, is used to determine the optimum α of a local $V_{X\alpha}$ potential

$$V_{X\alpha}(r) = -Z/r + \sum_c 2J_c - 3\alpha[3\rho_c(r)/8\pi]^{1/3} , \tag{11}$$

by requiring that

$$\langle 3d \mid V(\mathbf{r}) \mid 3d \rangle = \langle 3d \mid V_{X\alpha}(r) \mid 3d \rangle . \tag{12}$$

In Eq. (11), $\rho_c(r)$ is the core electron density. Now the model potential parameters are found by minimizing the deviation

$$\delta = \sum_i [V_{X\alpha}(r_i) - V_{\text{eff}}(r_i)]^2 . \tag{13}$$

In this work we have used an effective potential of the form 001, i.e., with $\mathcal{N}=3$ and $n(k)=0$, 0, and 1. This choice gives an asymptotic behavior of $V_{\text{eff}}(r)$ for $r=0$ very close to the correct limit

$$\lim_{r\to 0} [-rV_{\text{eff}}(r)] = Z . \tag{14}$$

For $3d$ atoms the computed limits differ from Z by 0.03 in the worst case. For $3d$ ions the agreement is about ten times better. This behavior is an important requirement for a correct calculation of ζ^0_{eff}, given the inner character of the $r^{-1}\partial V_{\text{eff}}(r)/\partial r$ operator.

In Huzinaga's approach, the substitution of the analytical core-valence interactions by a local model potential is complemented with an adequate reduction of the valence basis set. Accordingly, we use a reduced basis to compute the spin-orbit constants ζ^0_{eff} and ζ^* in Eq. (8). This small-basis calculation simulates the basis conditions of approximate cluster calculations. As reduced bases, we choose those in Ref. 23 having maximum overlap with Clementi and Roetti's multi-ζ bases.

RESULTS AND DISCUSSION

We will present results that show the usefulness of the effective core potential approach in the calculation of the atomic spin-orbit constants. In particular, we will compare complete spin-orbit constants, Eq. (6), with effective constants, Eq. (8). The former have been computed with large, high-quality basis sets. The latter with reduced bases as proposed in this work.

First, we recall that the $3d$-valence constant ζ^* is computed with the large basis in Eq. (6) and with the reduced basis in Eq. (8). This basis effect is the only difference between the accurate and the approximate calculation, as far as ζ^* is concerned, since we deal with a common definition for this quantity in both approaches. This difference turns out to be smaller than 2 cm^{-1} in all cases considered here, being smaller than 0.5 cm^{-1} in most systems. The reason for this negligible basis effect is double. First, since ζ^* is generally small (5–50 cm^{-1}), even an appreciable basis effect of about 10% would mean a variation of a few wave numbers. Furthermore, the Marvin radial integrals appearing in the definition of ζ^* are very accurately computed with the small basis. As examples, we present values for M^0 and M^2 for the neutral, dipositive, and tripositive $3d$ systems in Table I. The $3d$-$3d$ contribution to the spin-orbit constant is a function of these two direct-type radial integrals. Some extra exchange-type radial integrals appear in the $3d$-$4s$ contribution ζ^*_c (Ref. 8) but this constant is so small (less than 1 cm^{-1}) that any basis effect in its calculation would be entirely negligible.

In Table I we can see that the reduced bases give values

TABLE I. Radial integrals $M^0(3d,3d)$ and $M^2(3d,3d)$ (in cm^{-1}) for neutral (M^{0+}), dipositive, and tripositive $3d$ systems. *Note:* First and second row entries correspond to the high-quality bases of Ref. 21 and the reduced bases of Ref. 23, respectively. Third row entries are relative deviations (in %) between these two numbers.

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Radial integral $M^0(3d,3d)$										
M^{0+}	0.438	0.644	0.859	1.099	1.376	1.640	1.951	2.300	2.686	3.119
	0.432	0.637	0.850	1.087	1.361	1.621	1.926	2.269	2.649	3.074
	−1.37	−1.09	−1.05	−1.09	−1.09	−1.16	−1.28	−1.35	−1.38	−1.44
M^{2+}	0.513	0.709	0.922	1.160	1.436	1.704	2.030	2.367	2.756	3.190
	0.510	0.706	0.917	1.153	1.427	1.691	2.015	2.347	2.728	3.156
	−0.58	−0.42	−0.54	−0.60	−0.63	−0.76	−0.74	−0.84	−1.02	−1.07
M^{3+}		0.904	1.151	1.415	1.707	2.042	2.367	2.756	3.156	3.612
		0.902	1.148	1.412	1.702	2.035	2.357	2.744	3.139	3.592
		−0.22	−0.26	−0.21	−0.29	−0.34	−0.42	−0.44	−0.54	−0.55
Radial integral $M^2(3d,3d)$										
M^{0+}	0.237	0.350	0.468	0.598	0.750	0.894	1.064	1.253	1.464	1.701
	0.238	0.352	0.470	0.602	0.755	0.898	1.068	1.258	1.470	1.706
	0.42	0.57	0.43	0.67	0.67	0.45	0.38	0.40	0.41	0.29
M^{2+}	0.279	0.387	0.503	0.633	0.785	0.930	1.108	1.292	1.504	1.741
	0.281	0.389	0.506	0.639	0.789	0.935	1.114	1.298	1.511	1.748
	0.72	0.52	0.60	0.95	0.51	0.54	0.54	0.46	0.47	0.40
M^{3+}		0.498	0.634	0.780	0.940	1.124	1.301	1.514	1.733	1.982
		0.500	0.637	0.784	0.945	1.130	1.308	1.522	1.742	1.993
		0.40	0.47	0.51	0.53	0.53	0.54	0.53	0.52	0.55

of M^0 which differ by less than 1.5% from the Hartree-Fock results. Results for dipositive and tripositive cations, and for the radial integral M^2, are still better.

These numbers show that the relevant differences between the accurate and the approximate approach come from the value of the spin-own-orbit constant ζ_c^0. As noted above, the approximation to this quantity, ζ_{eff}^0 is affected by errors due to the use of effective core potentials and small bases. In Table II we present values of ζ_c^0 and ζ_{eff}^0 for neutral, dipositive, and tripositive $3d$ systems. In this table we observe that the differences between these calculations are smaller than 10 cm^{-1} for the neutral atoms, giving relative differences smaller than 5% of the spin-orbit constant. The agreement is particularly good on the right part of the period. Somewhat worse results appear for the cations, especially on the left of the period. We recall that this approximate calculation deviates from the analytical one by amounts comparable to the differences between the latter and the available experimental data. As the proposed approach has been developed to simulate a theoretical scheme, a direct comparison between the approximate method and these data is not particularly relevant here. However, we will see below that such a comparison is quite satisfactory.

It is interesting to analyze the very good agreement between ζ_{eff}^0 and ζ_c^0. In order to see the separate effects of the effective potential approximation and the use of reduced basis sets, we made two more hybrid calculations as described below. The combined results of all this numerical investigation are collected in Fig. 1, where line *A*

TABLE II. Values of ζ_c^0 (first row entries) and ζ_{eff}^0 (second row entries) (in cm^{-1}) for neutral, dipositive, and tripositive $3d$ systems. *Note:* Numbers in the third row are relative deviations (in %) between first and second rows entries.

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
M^{0+}	77	123	179	248	334	431	550	691	857	1051
	80	129	187	258	346	441	556	694	856	1043
	3.9	4.9	4.5	4.0	3.6	2.3	1.1	0.4	−0.1	−0.8
M^{2+}	86	131	187	256	343	441	563	703	869	1063
	96	145	205	277	367	466	591	729	891	1083
	11.6	10.7	9.6	8.2	7.0	5.7	5.0	3.7	2.5	1.9
M^{3+}		158	220	296	388	499	625	777	950	1154
		181	250	332	429	547	676	839	1008	1216
		14.6	13.6	12.2	10.6	9.6	8.2	8.0	6.1	5.4

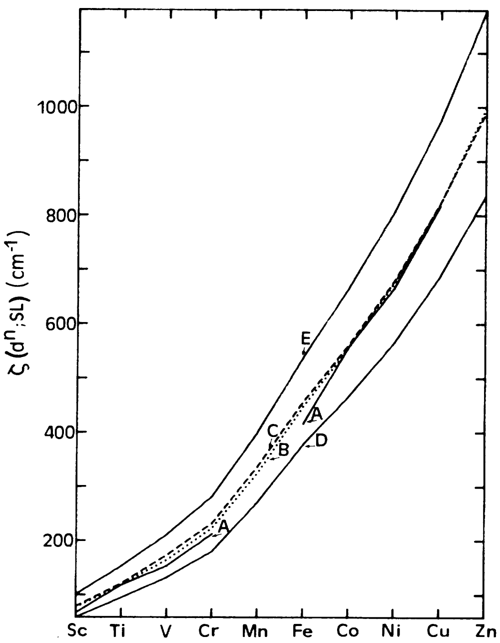

FIG. 1. Spin-orbit parameters (cm^{-1}) for the $3d$ atoms. *Note: A*, observed values, Refs. 3, 24, and 25; *B*, $\zeta(d^n;SL)$ with large bases; *C*, ζ_{eff} with reduced basis; *D*, $\zeta(d^n;SL)$ with reduced bases; *E*, ζ_{eff} with large bases.

represents the observed spin-orbit constants and lines *B* and *C*, $\zeta(d^n;SL)$ and ζ_{eff}, respectively. Line *D* corresponds to a calculation of $\zeta(d^n;SL)$ with reduced bases, and line *E* to a calculation of ζ_{eff} with the high-quality bases.

From the figure we observe, first, the well-known agreement between the analytical calculation and the observed data. Then we notice the more important result of this work, namely, the very good agreement between the approximate calculation and the analytical one. Comparison of lines *B* and *E* reveals that the model potential shields the nucleus less than the analytical interactions do, giving a more attractive central potential and larger spin-orbit constants. On the contrary, use of smaller valence basis sets in the calculation reduces the spin-orbit constants. This result confirms that very good overlap between the large and reduced bases[23] does not secure simulations of equivalent quality for the inner-core-$3d$ spin-orbit radial integrals, although, as seen above, the $3d$-$3d$ radial integrals are obtained with great accuracy in the reduced bases. The figure clearly shows that the method presented here is accurate because it contains a near cancellation of opposite errors. This circumstance makes it able to give reasonable values of spin-orbit constants in crystal calculations. In this context, it is interesting to notice that the model potentials of Ref. 20 give spin-orbit constants ζ^0_{eff} deviating at most a 4.5% from the corresponding values presented here.

The results of this work support the idea of computing nonempirically the spin-orbit constant of $3d$ ions in crystals in terms of atomic-type effective potentials and reduced basis sets. The splitting of the crystal multiplets could be obtained nonempirically in this way with a reasonable degree of confidence.

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