Electrostatically Correlated Spin-Orbit Interactions in l^N-Type Configurations*

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It is shown that, in second-order perturbation theory, electrostatically correlated spin-orbit interactions give rise to a "screening" of the spin-orbit coupling constant of an l^N-type configuration. In addition to this "screening" effect, these interactions also lead to an effective spin-other-orbit interaction which is not included in the usual empirical least-squares determination of the Coulomb and spin-orbit parameters. The consequences of this overt effect are discussed.

INTRODUCTION

IT has been a tradition among theoretical spectroscopists to treat the radial integrals that characterize the Coulomb and spin-orbit interactions within a particular configuration as parameters. These parameters have been deduced empirically by making least-squares fits of the calculated energy levels to the corresponding observed energy levels. In general, only the states of the particular configuration under study have been considered in the calculation of the energy matrices. Thus the effects of electrostatically correlated interactions with other configurations have been explicitly ignored. However, in deriving the parameters of a particular configuration by the method of least squares, it cannot be assumed that the parameters have not accommodated a large part of the effects of the electrostatically correlated interactions with other configurations. Furthermore, this implies that the eigenvectors resulting from the diagonalization of the energy matrices do not reflect the composition of the states of the configuration under study alone but will also represent contributions from the states of many other configurations. In the traditional empirical treatment only a few specific angular-dependent quantities are considered, namely, those of the Coulomb repulsion and the spin-orbit interaction within the configuration under study. Electrostatically correlated interactions that give rise to effects having a different angular dependence will not be adequately represented by the parameters of the configuration under study. We shall refer to these effects as "overt" since they may only be accommodated by introducing additional parameters. As part of a continuing study of the empirical calculation of energy levels we have endeavored to determine the angular dependence of these overt effects and to determine what electrostatically correlated interactions are included in the usual least-squares method.

The effects of weak electrostatic configuration interactions on the energy-level structure of l^N-type configurations have been considered in an earlier paper[1] (referred to here as I). However, in the heavy elements, especially the actinides, where spin-orbit interactions are appreciable,[2,3] the combined effects of spin-orbit and electrostatic configuration interactions should also be investigated. Since the spin-orbit interaction may be represented by a one-particle operator that is rigorously diagonal with respect to l but not n,[4] it will only couple nl^N with the configurations $nl^{N-1}n'l$, $n'l^{4l+1}nl^{N+1}$, and $n'l'^{4l'+1}nl^Nn''l'$. Inasmuch as these perturbing configurations will be energetically well-separated from the perturbed nl^N configuration it is a reasonable approximation to apply second-order perturbation theory as in I.

The bulk of these configuration interactions may be taken into account by modifying the energy matrices of nl^N in the same manner as in I. In the present paper an attempt is made to determine the angular dependence of these corrections. It is shown that the angular dependence of the correction may be represented by a sum of two terms, one proportional to the matrix elements of the spin-orbit interaction and the other to those of the spin-other-orbit interaction. In the usual determination of the Coulomb and spin-orbit parameters from experimental data by the method of least squares, the first term is absorbed as an effective "screening" of the spin-orbit coupling constant of the nl^N configuration. The second term, being an overt effect, is usually neglected in the least-squares analysis.

EXPRESSIONS FOR THE CONFIGURATION INTERACTIONS

The interacting configurations to be discussed differ only by the substitution of a single orbital of the same symmetry type and as a result it is necessary to consider both the one- and two-electron terms of the Hamiltonian. The Hamiltonian for an N-electron atom, with

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[1] K. Rajnak and B. G. Wybourne, Phys. Rev. **132**, 280 (1963).
[2] B. G. Wybourne, J. Chem. Phys. **36**, 2301 (1962).
[3] H. Lammermann and J. G. Conway, J. Chem. Phys. **38**, 259 (1963).
[4] E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra* (Cambridge University Press, New York, 1935).

the inclusion of spin-orbit interaction, may be written as

$$H=\sum_{i=1}^{N} H_i+\sum_{i>j=1}^{N} e^2/r_{ij}+\sum_{i=1}^{N} \xi(r_i)(\mathbf{s}_i\cdot\mathbf{l}_i), \quad (1)$$

where

$$H_i=-\frac{\hbar^2}{2m}\nabla_i^2-\frac{Ze^2}{r_i}. \quad (2)$$

The Hamiltonian may be divided into $H=H_0+H_1$ such that

$$H_0=\sum_{i=1}^{N}(H_i+v_i) \quad (3)$$

and

$$H_1=-\sum_{i=1}^{N} v_i+\sum_{i>j=1}^{N} e^2/r_{ij}+\sum_{i=1}^{N} \xi(r_i)(\mathbf{s}_i\cdot\mathbf{l}_i) \quad (4)$$

$$=-V+G+\Lambda,$$

where v_i is an average potential that acts on the ith electron and is chosen to minimize the energy E_1, while

$$V=\sum_{i=1}^{N} v_i, \quad G=\sum_{i>j=1}^{N} e^2/r_{ij}, \quad \text{and} \quad \Lambda=\sum_{i=1}^{N} \xi(r_i)(\mathbf{s}_i\cdot\mathbf{l}_i).$$

Using the notation of I, let two particular states, $(\alpha SLJ|$ and $|\alpha'S'L'J)$, of l^N be designated by $(\psi J|$ and $|\psi'J)$ and consider a perturbing state $|mJ)$ belonging to a particular perturbing configuration. Then the energy matrix for the l^N configuration will contain elements of the form

$$(l^N\psi J|H_1|l^N\psi'J). \quad (5)$$

Following Eq. (3) of I, the correction $C(\psi,\psi';J)$ to this matrix element, due to the effects of all the perturbing states $|mJ)$ of the perturbing configuration, may be written as the sum of six distinct terms, viz.,

$$C(\psi,\psi';J)=(-1/\Delta E_c)\sum_m (\psi J|H_1|mJ)(mJ|H_1|\psi'J)$$

$$=\sum_{x=1}^{6} C_x(\psi,\psi';J),$$

where

$$C_1(\psi,\psi';J)=(-1/\Delta E_c)\sum_m (\psi J|V|mJ)(mJ|V|\psi'J), \quad (6)$$

$$C_2(\psi,\psi';J)=(-1/\Delta E_c)\sum_m (\psi J|G|mJ)(mJ|G|\psi'J), \quad (7)$$

$$C_3(\psi,\psi';J)=(-1/\Delta E_c)\sum_m (\psi J|\Lambda|mJ)(mJ|\Lambda|\psi'J), \quad (8)$$

$$C_4(\psi,\psi';J)=(-2/\Delta E_c)\sum_m (\psi J|\Lambda|mJ)(mJ|G|\psi'J), \quad (9)$$

$$C_5(\psi,\psi';J)=(+2/\Delta E_c)\sum_m (\psi J|\Lambda|mJ)(mJ|V|\psi'J), \quad (10)$$

and

$$C_6(\psi,\psi';J)=(+2/\Delta E_c)\sum_m (\psi J|G|mJ)(mJ|V|\psi'J). \quad (11)$$

ΔE_c is a mean excitation energy and we have used the fact that the matrix elements are invariant with respect to interchange of ψ and ψ'.

The first correction term, Eq. (6), can only lead to a shift in the center of gravity of the nl^N configuration which in the usual parametrization will be absorbed in the $F^0(nlnl)$ parameter. The second term, Eq. (7), has been discussed in the previous paper. The third term, Eq. (8), represents the effect of configuration interaction induced solely by the spin-orbit interaction while the corrections of Eqs. (9) and (10) may be regarded as electrostatically correlated spin-orbit interactions between the configurations. The last correction term, Eq. (11), leads to a simple screening of the Slater F^k parameters of the l^N configuration without introducing any new angular-dependent factors. In the present paper we shall be concerned with the evaluation of the corrections represented by Eqs. (8), (9), and (10).

The summations over the perturbing states may be performed following the methods outlined in I and, as a result, we shall only sketch the derivations.

(A). nl^N with $nl^{N-1}n'l$

Noting that

$$(nl^N\alpha SLJ|\zeta(nl;n'l)\textstyle\sum_i(\mathbf{s}_i\cdot\mathbf{l}_i)|nl^{N-1}\alpha_1S_1L_1,n'sl;S''L''J)$$

$$=(-1)^{J+S+S''+S_1+L_1+l+s}\begin{Bmatrix} L & L'' & 1\\ S'' & S & J\end{Bmatrix}\begin{Bmatrix} L & L'' & 1\\ l & l & L_1\end{Bmatrix}\begin{Bmatrix} S & S'' & 1\\ s & s & S_1\end{Bmatrix}$$

$$\times[Ns(s+1)(2s+1)l(l+1)(2l+1)[S][L][S''][L'']]^{1/2}(l^N\psi\{|l^{N-1}\psi_1)\zeta(nl;n'l), \quad (12)$$

and using Eq. (39) of I, the summations in Eqs. (8) and (9) may be obtained as

$$C_3(\psi,\psi';J)=\frac{\zeta^2(nl,n'l)}{2\Delta E_c}\left[(l^N\psi J|\sum_{i=1}^{N}(\mathbf{s}_i\cdot\mathbf{l}_i)|l^N\psi'J)-\frac{Nl(l+1)}{2}\right], \quad (13)$$

and

$$C_4(\psi,\psi';J)=\frac{2\zeta(nl,n'l)}{\Delta E_c}\sum_k X^k\Big[(l^N\psi J|\sum_{i=1}^N(\mathbf{s}_i\cdot\mathbf{l}_i)|l^N\psi' J)/[l]$$
$$-\sum_t[t]\begin{Bmatrix}1&k&t\\l&l&l\end{Bmatrix}(-1)^{J+L'+S'}\begin{Bmatrix}L&L'&1\\S'&S&J\end{Bmatrix}[l(l+1)(2l+1)]^{1/2}\sum_{\tilde\psi}\begin{Bmatrix}\tilde L&L'&t\\1&k&L\end{Bmatrix}$$
$$\times(l^N\psi||\mathbf{U}^{(k)}||l^N\tilde\psi)(l^N\tilde\psi||\mathbf{V}^{(1t)}||l^N\psi')\Big], \quad (14)$$

where

$$\mathbf{V}^{(1t)}=\sum_{i=1}^N[\mathbf{s}_i^{(1)}\mathbf{u}_i^{(t)}], \quad (15)$$

and

$$X^k=(l||\mathbf{C}^{(k)}||l)^2R^k(nl,nl;nl,n'l). \quad (16)$$

The second part of Eq. (14) has the same angular dependence as the spin-other-orbit interaction[5] and hence gives rise to an overt effect. The term with $k=0$ in this part simplifies to

$$\frac{-2NR^0(nl,nl;nl,n'l)}{\Delta E_c}\zeta(nl;n'l)(l^N\psi J|\sum_{i=1}^N(\mathbf{s}_i\cdot\mathbf{l}_i)|l^N\psi' J). \quad (17)$$

To evaluate $C_5(\psi,\psi';J)$, we first note that

$$(nl^N\alpha SL|\sum_{i=1}^N v_i|nl^{N-1}\alpha_1S_1L_1n'l;SL)=N^{1/2}(\psi\{|\psi_1)(nl|v|n'l). \quad (18)$$

Summing over the perturbing states in Eq. (10) then yields

$$C_5(\psi,\psi';J)=(2/\Delta E_c)(l^N\psi J|\sum_{i=1}^N(\mathbf{s}_i\cdot\mathbf{l}_i)|l^N\psi' J)\zeta(nl;n'l)(nl|v|n'l). \quad (19)$$

Using Eqs. (13), (14), (17), and (19) we obtain the total corrections, $C_{SO}(\psi,\psi';J)$, to the spin-orbit matrix element $(l^N\psi J|\Lambda|l^N\psi' J)$ of the nl^N energy matrix for this particular perturbing configuration as

$$C_{SO}(\psi,\psi';J)=C_3(\psi,\psi';J)+C_4(\psi,\psi';J)+C_5(\psi,\psi';J)$$
$$=(\alpha+\beta)(l^N\psi J|\sum_{i=1}^N(\mathbf{s}_i\cdot\mathbf{l}_i)|l^N\psi' J)-\sum_{k>0,t}\gamma(k)[t]\begin{Bmatrix}1&k&t\\l&l&l\end{Bmatrix}(-1)^{J+L'+S'}\begin{Bmatrix}L&L'&1\\S'&S&J\end{Bmatrix}[l(l+1)(2l+1)]^{1/2}$$
$$\times\sum_{\tilde\psi}\begin{Bmatrix}\tilde L&L'&t\\1&k&L\end{Bmatrix}(l^N\psi||\mathbf{U}^{(k)}||l^N\tilde\psi)(l^N\tilde\psi||\mathbf{V}^{(1t)}||l^N\psi')-\delta N, \quad (20)$$

where

$$\alpha=\frac{\zeta(nl;n'l)}{\Delta E_c[l]}\Big[\frac{[l]}{2}\zeta(nl;n'l)+2\sum_{k>0}X^k\Big], \quad (21)$$

$$\beta=\frac{2\zeta(nl;n'l)}{\Delta E_c}[(1-N)R^0(nl,nl;nl,n'l)+(nl|v|n'l)], \quad (22)$$

$$\gamma(k)=(2X^k/\Delta E_c)\zeta(nl;n'l), \quad (23)$$

and

$$\delta=\frac{\zeta^2(nl;n'l)}{4\Delta E_c}l(l+1). \quad (24)$$

For the particular case of the nl^2 configuration the coefficients of fractional parentage in the expansions of the matrix elements of $\mathbf{U}^{(k)}$ and $\mathbf{V}^{(1t)}$ are unity and the sums over $\tilde\psi$ and t may be readily performed to yield

$$C(nl^2)=(l^2SLJ|\sum_{i=1}^2\mathbf{s}_i\cdot\mathbf{l}_i|l^2S'L'J)\Big[\alpha+\beta-2\sum_{k>0}\frac{\gamma(k)}{[l]}\Big]-2\delta. \quad (25)$$

[5] H. Horie, Progr. Theoret. Phys. (Kyoto) **10**, 296 (1953).

Thus, for the nl^2 configuration the effect of configuration mixing is simply to "screen" the spin-orbit coupling constant ζ_{nl}. For more than two electrons, however, the summation over $\tilde{\psi}$ is no longer tractable and a correction proportional to the angular dependence of the spin-other-orbit interaction should be added to the energy matrices of nl^N.

(B). nl^N with $n'l'^{4l+1}nl^{N+1}$

Using Eq. (44) of I, and noting that

$$(nl^{N+1}\psi_1 n'l'^{4l+1}\,{}^2l;S'L'J|\Lambda|nl^N\psi n'l'^{4l+2}\,{}^1S;SLJ)$$
$$=(-1)^{2S+S'+L+J+1}\begin{Bmatrix}L & L' & 1\\ S' & S & J\end{Bmatrix}\begin{Bmatrix}L & L' & 1\\ l & l & L_1\end{Bmatrix}\begin{Bmatrix}S & S' & 1\\ s & s & S_1\end{Bmatrix}$$
$$\times[(N+1)s(s+1)(2s+1)l(l+1)(2l+1)[S'][L'][S_1][L_1]]^{1/2}(l^{N+1}\psi_1\{|l^N\psi)\zeta(nl;n'l'), \quad (26)$$

a result that follows from Eq. (28) of Racah,[6] it may be shown that the resultant correction is identical in form with Eq. (20), apart from a linear shift of all the terms of the configuration. It should be noted that these types of interaction only arise in configurations nl^N with $n>l+1$. Thus they occur in the actinides ($5f^N$) but not in the corresponding lanthanides ($4f^N$).

(C). $nl^Nn'l'^{4l'+2}$ with $nl^Nn'l'^{4l'+1}n''l'$

It may be readily shown that[1]

$$(nl^N\alpha SL(n'l'^{4l'+1}n''l')\sigma\lambda;S'L'J|\Lambda|nl^N\alpha SLn'l'^{4l'+2}\,{}^1S;SLJ)$$
$$=(-1)^{J+L'+S}\delta(\sigma,1)\delta(\lambda,1)\begin{Bmatrix}L & L' & 1\\ S' & S & J\end{Bmatrix}[l'(l'+1)(2l'+1)s(s+1)(2s+1)[S'][L']]^{1/2}\frac{\zeta(n'l';n''l')}{3}. \quad (27)$$

Using this result, together with Eq. (33) of I, we find that the corrections $C_3(\psi,\psi';J)$ and $C_5(\psi,\psi';J)$ can at the most lead to a linear shift of the terms of the nl^N configuration. For $C_4(\psi,\psi';J)$ we have

$$C_4(\psi,\psi';J)=(l^N\alpha SLJ|\sum_{i=1}^{N}(\mathbf{s}_i\cdot\mathbf{l}_i)|l^N\alpha'S'L'J)\frac{\zeta(n'l';n''l')}{\Delta E_c}$$
$$\times\left[-2R^0(nln''l';n'lnl)\delta(l,l')+\sum_{k>0}(-1)^{l+l'}\frac{[k(k+1)-l(l+1)-l'(l'+1)]}{l(l+1)(2l+1)}X^k(nl,n''l';n'l'nl)\right]. \quad (28)$$

The occurrence of $(l+l')$ in the phase factor of the second part of Eq. (28) leads to both "screening" and "antiscreening" of the spin-orbit coupling constant ζ_{nl} of the l^N configuration but does not produce any overt effects. The term with $l=l'$ will arise in the actinides as the result of the excitation of a $4f$ electron from the $4f^{14}$ closed shell into the unfilled $6f$, or higher f, orbital.

DISCUSSION

It is apparent from the cases just considered that the spin-orbit parameters deduced from the least-squares fitting of energy levels will contain contributions from many configurations and cannot be considered as being associated purely with the l^N configuration. The "screening" produced by the mechanism of Eq. (8) is probably negligible due to the weakness of the coupling of the configurations by the spin-orbit interaction. However, the "screening" produced by the electrostatically correlated spin-orbit interactions of Eqs. (9) and (10) need not be negligible since if there is appreciable electrostatic coupling of the configurations these will more than offset the weakness of the spin-orbit coupling. The magnitude of this screening will be largely determined by the radial factor,

$$[(1-N)R^0(nl,nl;nl,n'l')+(nl|v|n'l')], \quad (29)$$

appearing in Eq. (22). The size of this factor will depend upon the choice of zero-order wave functions and the form of the average potential v which is used. Until the necessary radial integrals have been computed for several specific cases, however, it is difficult to make any general statements about magnitude of the screening.

The appearance of a term proportional to the spin-other-orbit interaction will lead to overt effects which the usual parameters will be unable to adequately accommodate. In the limit of LS coupling this interaction will not produce deviations from the Lande interval[4] rule but would lead to a different spin-orbit coupling constant for each multiplet. These overt effects could be included by introducing l additional parameters. It

[6] G. Racah, Phys. Rev. **63**, 367 (1943).

should be noted that due to the presence of these overt effects a spin-orbit coupling constant deduced from a single multiplet that follows the Lande interval rule need not be representative of the entire configuration.

When the parameters are derived from a least-squares method it is impossible to distinguish the contributions to the spin-orbit coupling constant that arise from the effects of electrostatically correlated interactions with other configurations and those that arise from the spin-orbit interactions within the configuration. Likewise, in empirical determinations of the spin-other-orbit interactions for a configuration, it is impossible to decide whether the derived spin-other-orbit parameters represent a real spin-other-orbit interaction within the configuration or whether they are attributable to a pseudo-spin-other-orbit interaction that arises out of the effects of electrostatically correlated spin-orbit interactions.

Electrostatically correlated spin-orbit interactions are by no means the only possible correlated interactions that couple configurations. In fact, these interactions are probably of lesser significance than the electrostatically correlated two-particle orbit-orbit, spin-spin, and spin-other-orbit interactions between configurations. The properties of these interactions will be taken up in a later paper.

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Nonadiabatic Theory of Inelastic Electron-Hydrogen Scattering*

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The nonadiabatic theory is applied to the inelastic S-wave scattering of low-energy electrons from atomic hydrogen. The zeroth-order (angle-independent) approximation for excitation of the $2s$ level from the ground state is described by the same equation used to describe elastic scattering below the $2s$ threshold, but with more complicated boundary conditions. The solution has been effected by expanding the wave function in terms of separable solutions. With the assumption of reciprocity it is also possible to obtain the $2s-2s$ cross sections. The elastic $(1s-1s)$ cross sections are within 1% of the close-coupling results in the triplet case, but are about 20% greater in the singlet case. The inelastic $(1s-2s)$ cross sections are reduced about 20% in the triplet case and 20 to 40% in the singlet case, relative to the close-coupling results.

I. INTRODUCTION

IN previous papers[1] a nonadiabatic theory of elastic scattering has been developed and applied, among other things, to the low-energy scattering of electrons from atomic hydrogen. At present the theory is being extended to cover inelastic S-wave scattering, and hence obtain the scattering cross sections σ_{1s-1s} and σ_{1s-2s} above the $2s$ excitation threshold. This paper deals with the solution of the zeroth-order (angle-independent or relative s wave) problem described in Sec. II of this paper. Only a brief review of the nonadiabatic theory is given since a full description is to be found in I. As pointed out in Sec. III, the elastic scattering cross section σ_{2s-2s} may also be found from our calculation if it is assumed that the reciprocity condition is fulfilled.

The accuracy of the solution is discussed in Secs. IV and V. In Sec. VI the nonadiabatic results are presented and compared with the results from the $1s-2s$ close-coupling expansion.[2-5] The latter has been shown to be a variational approximate solution of the zeroth-order problem.[1] Finally, the implication of our results for both the experimental and theoretical determination of the total inelastic cross section, σ_{1s-2s} is discussed in Sec. VII.

II. ZEROTH-ORDER NONADIABATIC THEORY

It will be recalled from I that the nonadiabatic theory starts with a decomposition of the S-wave function

$$\Psi(r_1r_2\theta_{12})=1/r_1r_2\sum_{l=0}(2l+1)^{1/2}\Phi_l(r_1r_2)P_l(\cos\theta_{12}), \quad \text{(I2.3)}$$

from which by substitution into the Schrödinger equa-

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[1] A. Temkin, Phys. Rev. Letters **4**, 566 (1960); Phys. Rev. **126**, 130 (1962). The latter paper will be referred to as I in the text. Equations referring to it will be prefixed by a I.

[2] R. Marriott, Proc. Phys. Soc. (London) **72**, 121 (1958).

[3] P. G. Burke, H. M. Schey, and K. Smith, Phys. Rev. **129**, 1258 (1963).

[4] K. Omidvar, in *Proceedings of the Third International Conference on the Physics of Electronic and Atomic Collisions* (North-Holland Publishing Company, Amsterdam, to be published). Dr. Omidvar has kindly calculated for us the $1s$–$2s$ close-coupling results just above threshold. Cf. also, K. Omidvar, Phys. Rev. **133**, A970 (1964).

[5] R. Damburg and R. Peterkop, Proc. Phys. Soc. (London) **80**, 1073 (1962).