Spin–spin coupling and mixing of 1sns ³S₁ and 1sn'd ³D₁ helium levels

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Off-diagonal matrix elements $\langle 1sns\ ^3S_1|H_{e,ss}|1sn'd\ ^3D_1\rangle$ $(n,n'=3-10)$, which determine the mixing of $1sn\ s^3S_1$ and $1sn'd\ ^3D_1$ levels in neutral helium have been estimated analytically. We have demonstrated that the matrix elements are nonzero if the spin–spin part $(H_{e,ss})$ of the full Breit–Pauli Hamiltonian is used. The basis is composed of antisymmetrized products of hydrogen-like electron functions in the Coulomb field of a nucleus. A technique has been developed to get rid of divergence in calculating matrix elements including radial wave functions. © *1996 American Institute of Physics.* [S1063-7761(96)00709-3]

1. INTRODUCTION

In processing measurements of energy gaps in the helium fine structure, the researchers often use a semiempirical approach in which a recorded spectrum is interpreted in terms of averaged atomic Hamiltonian parameters with due account of both spin-dependent and spin-independent relativistic corrections proportional to α^2Ry,[1,2] where α is the fine-structure constant. This approach seems preferable because the spectral characteristics are expressed in terms of several parameters which are, in fact, reduced matrix elements of the Hamiltonian and can be calculated in advance using accurate variational and Hartree–Fock techniques.

The limitations of this approach are primarily caused by the selection of the initial basis for the atomic Hamiltonian. The Hamiltonian, in particular, is assumed to be diagonal with respect to the total orbital momentum, this means that the total orbital momentum L is presumed to be a "good" quantum number.

In interpreting accurate measurements of fine-structure energies, however, an adequate interpretation of measurements may be possible in some cases only when the mixing of states with different L and equal parity is taken into account. This issue was discussed by Kaiser and von Oppen,[3] who studied the singlet–triplet anticrossing of the Stark components of the $1s3d$ level in neutral helium.

The goal of this work was to estimate analytically nondiagonal matrix elements of the spin-spin coupling operator, $\langle 1sns\ ^3S_1|H_{e,ss}|1sn'd\ ^3D_1\rangle$ $(n,n'=3-10)$, which determines the mixing constants in the expansions

$$|1\rangle = \cos\theta|1sns\ ^3S_1\rangle + \sin\theta|1sn'd\ ^3D_1\rangle,$$

$$|2\rangle = -\sin\theta|1sns\ ^3S_1\rangle + \cos\theta|1sn'd\ ^3D_1\rangle, \tag{1}$$

where $|1\rangle$, $|2\rangle$ are the eigenstates of the total atomic Hamiltonian and θ is the mixing angle between the $1sns\ ^3S_1$ and $1sn'd\ ^3D_1$ states.

2. ANALYTIC CALCULATIONS OF OFF-DIAGONAL MATRIX ELEMENTS IN THE LS-COUPLING SCHEME

In this work the perturbation operator generating nonzero off-diagonal matrix elements coupling the states with the orbital momentum L and $L\pm2$ is the operator of spin–spin coupling $H_{e,ss}$ in the Breit–Pauli Hamiltonian[4] in the form of a scalar product of irreducible second-rank tensors:[5]

$$H_{e,ss}=\frac{\alpha^2}{r_{12}^3}\left[\mathbf{S}_1\mathbf{S}_2-\frac{3}{r_{12}^2}(\mathbf{S}_1\mathbf{r}_{12})(\mathbf{S}_2\mathbf{r}_{12})\right]=S^{(2)}\cdot L^{(2)}. \tag{2}$$

Equation (2) does not include the term with the delta-function responsible for the contact interaction because its contribution to the energy of triplet states is zero. An important point is that Heisenberg's hydrogen-like approximation[4] cannot be applied to the basis wave functions in this case because it leads to zero off-diagonal matrix elements by virtue of the identity

$$\int_0^\infty g_{nl}(r)g_{nl\pm2}(r)\frac{dr}{r}=0 \tag{3}$$

for the corresponding radial integrals. Here $g_{nl}(r)$ is the radial wave function of a hydrogen-like atom.[4] Therefore we took for the basis the antisymmetrized product of electron wave functions in the Coulomb potential of a nucleus with the charge $Z=2$ (Z is the nuclear charge) in the LS-coupling scheme. The corresponding reduced matrix element is determined by the equation[5-7]

$$\langle L'S'J'M'|S^{(2)}\cdot L^{(2)}|LSJM\rangle$$

$$=(-1)^{L+S'+J}\delta_{J,J'}\delta_{M,M'}\begin{Bmatrix}J & S' & L' \\ 2 & L & S\end{Bmatrix}\langle L'||L^{(2)}||L\rangle$$

$$\times\langle S'||S^{(2)}||S\rangle, \tag{4}$$

where J and M are the total angular momentum and its projection, and respectively,

$$\begin{Bmatrix}a & b & c \\ d & e & f\end{Bmatrix}$$

is Wigner's $6j$-symbol.[6] The integration with respect to angles is performed using standard relations of the algebra of angular momenta[6,8] and it presents no great difficulty. On the contrary, the calculation of radial integrals is difficult because of nonphysical divergence due to the cofactor $1/r_{12}^5$ in the integrands. The methods for eliminating this divergence are usually based on recursion relations for Legendre polynomials and Gauss's hypergeometric functions, which emerge in the process of integration with respect to the radial variables.[9,10]

We propose an alternative technique for getting rid of the divergence prior to the integration with respect to the radial variables. First of all, let us expand the function $1/r_{12}^5$ in terms of spherical harmonics, which allows us to separate the radial and angular variables:[6]

$$\frac{1}{r_{12}^5} = \sum_{lm} q_l(r_>,r_<)Y_{lm}^*(\mathbf{n}_1)Y_{lm}(\mathbf{n}_2),$$
(5)

$$q_l(r_>,r_<) = \frac{\pi}{3(r_>^2 - r_<^2)^3}(2l-1)(2l+3)\frac{r_<^l}{r_>^{l+1}}$$
$$\times\left(\frac{r_>^2}{2l-1} - \frac{r_<^2}{2l+3}\right),$$

where $r_<$ ($r_>$) denotes the smaller (larger) value of r_1 and r_2, and $Y_{lm}(\mathbf{n})$ is a spherical harmonic.

By using Eq. (5) and omitting the constant factor due to the integration with respect to the angles, we obtain the following expression for the radial component of the spin–spin coupling:

$$H_{e,ss}^{\mathrm{rad}}(r_>,r_<)$$

$$=\begin{cases} r_1^2 q_0(r_>,r_<) + r_2^2 q_2(r_>,r_<) - 2r_1 r_2 q_1(r_>,r_<), & (6a) \\ r_1^2 q_2(r_>,r_<) + r_2^2 q_0(r_>,r_< - 2r_1 r_2 q_1(r_>,r_<). & (6b) \end{cases}$$

The upper (a) and the lower (b) lines correspond to the direct and exchange interaction, respectively. By substituting Eq. (5) into (6a). and (6b), one can easily prove that the expression in the upper line equals $1/r_1^3$ if $r_1 > r_2$ and zero if $r_1 < r_2$, and the expression in the lower line equals zero and $1/r_2^3$, respectively, for the same conditions for the radial variables. These results allow us to unify and simplify the procedure for calculating the radial integrals

$$\int_0^\infty \int_0^\infty r_1^2 r_2^2 \Phi(r_1,r_2) H_{e,ss}^{\mathrm{rad}}(r_>,r_<)dr_1 dr_2$$

$$= \int_0^\infty r_1^2\left\{\int_0^{r_1} r_2^2 H_{e,ss}^{\mathrm{rad}}(r_1,r_2)\Phi(r_1,r_2)dr_2\right.$$

$$\left. + \int_{r_1}^\infty r_2^2 H_{e,ss}^{\mathrm{rad}}(r_2,r_1)\Phi(r_1,r_2)dr_2\right\}dr_1,$$
(7)

$$\Phi(r_1,r_2)=\begin{cases} g_{n0}(r_1)g_{n2}(r_1)g_{10}(r_2)g_{10}(r_2) \\ \text{(direct Coulomb interaction)}, \\ g_{n0}(r_1)g_{10}(r_1)g_{10}(r_2)g_{n2}(r_2) \\ \text{(exchange interaction)}. \end{cases}$$
(8)

After these transformations performed on $H_{e,ss}^{\mathrm{rad}}(r_>,r_<)$, the radial integrals in Eq. (7) do not diverge, and the integration with respect to radial variables can be performed analytically.[11]

We demonstrate as a example the final expression for the off-diagonal matrix element $\langle 1s3s\ ^3S_1|H_{e,ss}|1s3d^3D_1\rangle$ which contains only the term of the lowest order in α and Z:

$$\langle 1s3s^3S_1|H_{e,ss}|1s3d^3D_1\rangle = -\frac{5\sqrt{5}}{2^{12}\cdot 3}\alpha^2 Z^3 \text{ a.u.}$$

$$= -2.5503 \text{ GHz.}$$
(9)

This result is very close to the value numerically calculated by Drake,[12,13] who took account of the relativistic correction proportional to $(\alpha Z)^2$:

$$\langle 1s3s^3S_1|H_{e,ss}|1s3d^3D_1\rangle = -9.0972\cdot 10^{-4}\alpha^2 Z^3 \text{ a.u.}$$

$$= -2.5499 \text{ GHz.}$$
(10)

Similar calculations of off-diagonal elements $\langle 1sns^3S_1|H_{e,ss}|1sn'd^3D_1\rangle$ with $n,n'=3-10$ are given in Fig. 1 and Table I. The graph indicates, in particular, that the off-diagonal elements are functions of both n and n' and at a fixed n' drop by a factor of about ten as n changes from 3 to 10.

3. DISCUSSION

The technique proposed in this paper can be applied, naturally, only to approximate estimates of parameters of
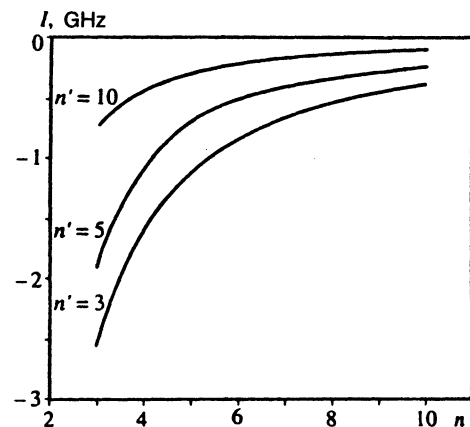

FIG. 1. Off-diagonal matrix elements $I=\langle 1sns^3S_1|H_{e,ss}|1sn'd^3D_1\rangle$ in neutral helium versus n at $n'=3,5,10$ and n ranging between 3 and 10.

TABLE I. Nondiagonal matrix elements $\langle 1sns\,{}^3S_1|H_{e,ss}|1sn'd\,{}^3D_1\rangle$ (GHz) in helium.

n	n'							
	3	4	5	6	7	8	9	10
3	-2.5503	-2.4674	-1.9023	-1.4910	-1.2015	-0.99235	-0.83651	-0.71710
4	-1.5850	-1.2511	-1.0695	-0.86145	-0.70306	-0.58486	-0.49525	-0.42585
5	-1.1069	-0.87480	-0.67800	-0.56767	-0.46883	-0.39237	-0.33345	-0.28740
6	-0.83104	-0.65547	-0.50878	-0.40364	-0.33933	-0.28564	-0.24350	-0.21028
7	-0.65430	-0.51542	-0.39970	-0.31751	-0.25837	-0.21954	-0.18774	-0.16241
8	-0.53282	-0.41939	-0.32500	-0.25806	-0.21021	-0.17488	-0.15037	-0.13032
9	-0.44498	-0.35006	-0.27115	-0.21521	-0.17527	-0.14594	-0.12368	-0.10756
10	-0.37899	-0.29804	-0.23078	-0.18312	-0.14910	-0.12413	-0.10527	-0.090607

helium spectra. Our calculations in the Hartree–Fock approximation using the multiconfigurational approach yield the following result:

$$\langle 1s3s^3S_1|H_{e,ss}|1s3d^3D_1\rangle = -8.130\cdot 10^{-4}\alpha^2 Z^3 \text{a.u.}$$
$$= -2.278 \text{ GHz.} \qquad (11)$$

The difference between numerical values in Eqs. (9) and (11) is 0.2723 GHz and is caused by neglecting correlation effects when we have used the hydrogen-like functions in the derivation of Eq. (9). The more accurate calculation based on the variational approach with many parameters yields[1)]

$$\langle 1s3s^3S_1|H_{e,ss}|1s3d^3D_1\rangle = -7.4373153$$
$$\times 10^{-4}\alpha^2 Z^3 \text{ a.u.}$$

The higher-order corrections, which also yield nonzero contributions to the off-diagonal matrix elements, may be classified with two types. The first type includes corrections which tend to a nonzero value as $M\to\infty$, where M is the nucleus mass. The corrections of the second type are due to the finite nucleus mass. The corrections of the first type proportional to α^3Ry are due to the contribution of the anomalous magnetic moment of electron (the Schwinger correction) to the two-particle Hamiltonian. If the spin-dependent component of the Breit–Pauli Hamiltonian is presented in the form

$$H = H_{Z,so} + H_{e,so} + H_{e,ss}, \qquad (12)$$

where $H_{Z,so}$ is the spin–orbit interaction with the nucleus, $H_{e,so}$ is the spin–orbit interaction between the electrons, and $H_{e,ss}$ is the spin–spin coupling defined by Eq. (2), the correction H^{anom} due to the anomalous magnetic moment of electron is determined by the formula[14]

$$H^{\text{anom}} = \frac{\alpha}{2\pi}\left(2H_{Z,so} + \frac{4}{3}H_{e,so} + 2H_{e,ss}\right). \qquad (13)$$

The corrections H_M of the second type are due to the effects of radiative "recoil" of a nucleus of a finite mass:[15]

$$H_M = -\frac{m_e}{M}\left(H_{Z,so} + 3H_{e,so} + 3H_{e,ss} - \frac{Z\alpha^2}{r_1^3}\right.$$
$$\left.\times\sigma_1[\mathbf{r}_1\mathbf{p}_2]\right). \qquad (14)$$

Here σ_1 and $\mathbf{p}_i$ are the spin and momentum of the ith electron, m_e is the electron mass. It is obvious that nonzero off-diagonal matrix elements are only due to the spin–spin components of the Hamiltonian in Eq. (12) and defined by Eqs. (13) and (14), and the corrections to the larger numerical value in Eq. (9) are proportional to α and m_e/M.

In conclusion, we would like to stress once again that, although the mixing of the states $1sns^3S_1$ and $1sn'd^3D_1$ is small (specifically, the mixing angle between the states $1s3s^3S_1$ and $1s3d^3D_1$ introduced in Eq. (1) is $\theta\approx 0.000003$), this effect is fundamentally important for interpreting precise measurements of helium spectral parameters.[3] On the other hand, the mixing of levels with the orbital momenta L and $L\pm 2$ may be important in the search for effects of parity violation in neutral helium[16] and in helium-like ions with a small charge[17] in the anticrossing of levels under electromagnetic field. Finally, the mixing of levels with different orbital momenta and equal parities is proportional to Z^3 and may be interesting for the high-resolution spectroscopy of multiply charged high Z ions.[18,19]

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