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Calculation of the fine structure of the $a\,^3\Sigma_u^+$ state of molecular helium[*]

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Using a published correlated wave function computed by Poshusta and Matsen, we have obtained a vibrationally averaged first-order spin-spin constant of -0.04089 cm^{-1} for the $a\,^3\Sigma_u^+$ metastable state of molecular helium. This is in good agreement with the experimental value of -0.0367 cm^{-1} recently reported by Lichten *et al*. Our results strongly suggest that second-order spin-orbit effects are small.

The spin-spin constant λ' of He_2 $a\,^3\Sigma_u^+$, which essentially determines the fine structure of this state, has recently been deduced experimentally by Lichten and co-workers[1,2] to be -0.0367 cm^{-1}. This value is an order of magnitude smaller and opposite in sign to values of other Σ states deduced semiempirically[3] for systems which had been previously studied experimentally such as $N_2\,^3\Sigma_u^+$,[4] $NH\,^3\Sigma^-$,[5] O_2 $X\,^3\Sigma_g^-$,[6] $SO\,^3\Sigma^-$,[7] $S_2\,^3\Sigma^-$,[8] and $SeO\,^3\Sigma^-$.[9]

Experimental results on He_2 have been limited to the gross structure of Rydberg-like states.[10] Scattering experimentalists have been interested in the potential-energy surface of the $a\,^3\Sigma_u^+$ state due to the possible existence of a barrier beyond the minimum.[11] This has stimulated accurate calculations for this wave function[11] and one of them, that of Poshusta and Matsen,[12] is utilized here.

The theoretical value reported here for λ' is -0.04089 cm^{-1}, in good agreement with experiment. The analysis of our calculations, which hopefully can provide insight into more complex molecules, shows that: (i) The fine-structure splitting of the He_2 $a\,^3\Sigma_u^+$ state is determined by the first-order spin-spin constant λ', contributions to which come mainly from σ orbitals, and to a much lesser degree from π orbitals. (ii) The contributions to the fine-structure splitting of the He_2 $a\,^3\Sigma_u^+$ state of second-order spin-orbit coupling, the spin-rotation coupling, and the corrections of Schlapp[13] are negligible.

Theoretical investigations of spin-dependent operators in molecules have been carried out by van der Avoird and Wormer,[14] Chiu,[15] Chiu,[16] Fontana,[17] Matcha and co-workers,[18] and Walker and Richards,[19] for example. The general theory for the evaluation of reduced matrix elements in molecules has been discussed by Cooper, Musher, and Walker.[20] Much quantitative work on diagonal and off-diagonal spin-dependent matrix elements has been carried out for atoms by Beck,[21] Blume and Watson,[22] Froese-Fischer,[23] Lo *et al.*,[24] Malli,[25] and Nicolaides,[26] for example. For our calculations, which in effect involve two open-shell electrons, we have utilized the expressions of Judd[27] and Carrington *et al.*[28]

I. FIRST-ORDER SPIN-SPIN CONSTANT

The total wave function for a given rotational state, within the Born-Oppenheimer approximation in Hund's case *b*, is the product of a vibrational wave function, and an electronic-rotational wave function. For Σ states, the latter is also a product function. For molecular helium of atomic mass four, the nuclear spin is zero, J represents the total angular momentum of the molecule, and only odd rotational levels (K) are present.

The spin-spin interaction energy H_{ss} is (in a.u.)

$$H_{ss} = \alpha^2 \sum_{i<j} \left(\frac{(\vec{s}_i \cdot \vec{s}_j)}{r_{ij}^3} - \frac{3(\vec{s}_i \cdot \vec{r}_{ij})(\vec{s}_j \cdot \vec{r}_{ij})}{r_{ij}^5} \right) \qquad (1)$$

in the space-fixed system. The contact part of the spin-spin interaction does not contribute to the splitting. The first-order spin-spin contribution to the fine-structure splitting is given by the matrix element

$$\langle v\Lambda K S J | H_{ss} | v\Lambda K S J \rangle .$$

The quantum number v refers to the vibrational state, and Λ is the z component of $\vec{K}$ in the molecular system. Utilizing the results of Judd[27] and Carrington *et al.*,[28] which involve application of the Wigner-Eckart theorem, and transformation of a second-order spherical harmonic from the space-fixed system to the molecular system, we obtain

$$\langle \nu\Lambda K S J | H_{ss} | \nu' \Lambda' K' S' J' \rangle = \delta_{J,J'} [(2K+1)(2K'+1)]^{1/2} (-1)^{J+\Sigma-\Lambda'} \begin{Bmatrix} K & K' & 2 \\ S' & S & J \end{Bmatrix} \begin{pmatrix} K' & 2 & K \\ \Lambda' & \Lambda-\Lambda' & -\Lambda \end{pmatrix}$$
$$\times \langle \nu\Lambda S\Sigma | H'_{ss} | \nu' \Lambda' S' \Sigma' = \Sigma+\Lambda-\Lambda' \rangle \Big/ \begin{pmatrix} S & 2 & S' \\ -\Sigma & \Lambda'-\Lambda & \Sigma+\Lambda-\Lambda' \end{pmatrix}, \qquad (2)$$

where the K and J dependence is given explicitly. For the case of interest, $\Lambda' = \Lambda$ and $S = S'$ so the spin $3j$ symbol does not vanish. The electronic matrix element is written as the product of $\lambda'(R)$ and a function of Σ,

$$\langle \Lambda S\Sigma | H'_{ss} | \Lambda S\Sigma \rangle = \tfrac{2}{3} \lambda'(R) [3\Sigma^2 - S(S+1)]. \qquad (3)$$

It is well known that it is very difficult to obtain theoretical potential-energy surfaces in good quantitative agreement with experiment.[11,29] However, for atoms, properties other than total energies (especially one-particle properties), frequently place less stringent demands on the wave function.[30] There is some evidence that this may be true for the spin-spin constant of O_2 [31] and the analysis of this section strongly suggests that this is the case in He_2 as well.

To evaluate the spin-spin constant λ', we used a considerably sophisticated Slater-type-orbital (STO) wave function[11]:

$$\psi(a\,^3\Sigma_u^+) = \sum_{i=0}^{11} C_i \psi_i \,. \qquad (4)$$

The ψ_i's given in Table I are built from bond functions $[(ab)cd]$, where just a and b have been bonded.[32] In terms of Slater determinants, we have

$$[(ab)cd] = A[a(1)\alpha(1),\ c(2)\alpha(2),\ b(3)\beta(3),\ d(4)\beta(4)] + A[b(1)\alpha(1),\ c(2)\alpha(2),\ a(3)\beta(3),\ d(4)\beta(4)]$$
$$+ A[a(1)\alpha(1),\ d(2)\alpha(2),\ c(3)\beta(3),\ b(4)\beta(4)] + A[b(1)\alpha(1),\ d(2)\alpha(2),\ c(3)\beta(3),\ a(4)\beta(4)], \qquad (5)$$

where A is the four-electron antisymmetrizer and a, b, c, d are normalized STO's centered on one of the nuclei. Such bond functions are automatically eigenstates of S^2, S_z, and L_z. The projection operator $\vec{P}$ produces the *ungerade* and + symmetries.

We consider the evaluation of matrix elements which involve nonorthogonal functions. Because of the highly overlapped functions, the expansion coefficients[12] have no obvious meaning. A determinantal matrix element is given by[33]

$$\langle \Delta_B | \sum_{k<l} g_{kl} | \Delta_A \rangle$$
$$= (\det\vec{U})(\det\vec{V}^\dagger) \sum_{i<j} \prod_{m\neq i,j} \hat{d}_{mm} \langle \hat{b}_i(1) \hat{b}_j(2) |$$
$$\times g_{12} (1 - \vec{P}_{12}) | \hat{a}_i(1) \hat{a}_j(2) \rangle . \qquad (6)$$

Δ_A and Δ_B are two Slater determinants having spin-orbital sets $\{a_i\}$ and $\{b_i\}$ which are internally orthonormal and unitarily transformed to the sets $\{\hat{a}_i\}$ and $\{\hat{b}_i\}$ by $\vec{V}$ and $\vec{U}$. If the overlap matrix is given by $D_{ij} = \langle b_i | a_j \rangle$ then $\vec{U}$ and $\vec{V}$ are eigenvectors of $\vec{D}\vec{D}^\dagger$ and $\vec{D}^\dagger\vec{D}$, respectively, and $\vec{d}$ is the positive square root of the eigenvalues of $\vec{D}^\dagger\vec{D}$.

The two-electron matrix elements of Eq. (6) are evaluated using the programs of Pritchard *et al.*,[34] recognizing that the $2p_{0b}$ and $3d_{\pm 1b}$ STO's of Table I have opposite signs to those required in the integral routines owing to the differing b-centered coordinate systems.[12,18,35]

The configuration-interaction (CI) calculation was carried out with the first seven configurations to give

$$\lambda'(R) = -0.03525 \text{ cm}^{-1}$$

at $R = 2.015$ a.u. The dominant configuration, ψ_0, contributes -0.04125 cm^{-1}. First-order perturba-

TABLE I. Configurations of $\psi(a\,^3\Sigma_u^+)$. The P's are symmetry projection operators and primes distinguish different STO exponents. Complete details are found in Ref. 12.

n	ψ_n
0	$P[(1s_a 1s_a) 2s'_b 1s'_b]$
1	$2P[(1s_a 2s_a) 2s'_b 1s'_b]$
2	$P[(2s_a 2s_a) 2s'_b 1s'_b]$
3	$P[(1s_a 1s_a) 2s_a 1s'_b]$
4	$P[(1s_a 1s_a) 2p'_{0b} 1s'_b]$
5	$2P[(1s_a 2p_{0a}) 1s'_b 2s'_b]$
6	$P[(1s_a 1s_a) 2p_{0a} 1s'_b]$
7	$P[(2p_{0a} 2p_{0a}) 2s'_b 1s'_b]$
8	$P[(1s_a 1s_a) 3s'_b 2s'_b]$
9	$P[(3d_{0a} 3d_{0a}) 1s'_b 2s'_b]$
10	$2P[(2p_{+1a} 2p_{-1a}) 1s'_b 2s'_b]$
11	$2P\{-[(3d_{-1a} 3d_{+1a}) 1s'_b 2s'_b] + [(3d_{-2a} 3d_{+2a}) 1s'_b 2s'_b]\}$

TABLE II. Individual contributions to $\lambda'(R)$ at $R=2.015$ from the two-particle STO integrals, $\langle \omega_i(1)\omega_j(2)|g_{ss}(1,2)|\omega_{k(1)}\omega_{l(2)}\rangle$.

Name	Restrictions	Contribution (cm^{-1})
One-center	i, j, k, l on same center	−0.000 12
Coulomb	i, k on same center; j, l on same, but different center	−0.093 92
Exchange	i, k (j, l) on different centers	−0.011 53
Hybrid	three of i, j, k, l on same center	+0.069 96
Total		−0.035 59

tion theory, for which the perturbative contributions to λ' are proportional to $\langle 2\delta\psi_i|H'_{ss}|\psi_0\rangle$, yields −0.03519 cm^{-1}. The individual contributions are +0.00249, +0.00147, +0.00676, +0.00215, −0.00316, and −0.00366 cm^{-1}, respectively. Note that the corrections to the basis set are added perturbatively to the zeroth-order wave function. This is similar to the procedure of Nakatsuji and Musher,[36] which adds d orbitals perturbatively.

In Table II, we give the contributions of the STO Coulomb, exchange, hybrid and one-center integrals to $\lambda'(R)$, for $R=2.015$. It can be seen that all two-center integrals give sizable contributions, while the one-center contributions are negligible. In the qualitative model introduced previously,[1] the hybrid terms were assumed to be negligible.

The values of $\lambda'(R)$ as a function of R are given in Table III. The CI computation time per value of R was 7 min on the NYU-AEC CDC 6600, in contrast to the estimated time of 1 h for the full wave function.

When R approaches zero, all but ψ_4, ψ_5, and ψ_6 vanish, and the molecular state becomes the $M_L=0$, $M_S=1$, $1s^2 2s2p\,^3P^0$ state of Be I. We point out that for such a limiting procedure to be valid, the wave function must contain the essential united atom configurations and be optimized as regards both STO exponents and mixing coefficients as $R \rightarrow 0$. We obtain the value of λ' at $R=0$, −0.092 cm^{-1} from the measured fine-structure separations,[37] using the relationship[21]

$$W_J = X + AJ(J+1) - \tfrac{1}{2}\lambda' J^2(J+1)^2\,. \qquad (7)$$

The calculated value of −0.09539 cm^{-1} at $R=1.500$ is larger than this. Since λ' at $R=1.500$ is still dominated by the purely molecular contributions from σ orbitals, we expect that $\lambda'(R)$ may increase somewhat, then decrease to its atomic value as R decreases.

We used a simple harmonic-oscillator wave function for the ground vibrational state, centered at the equilibrium distance,[10] to perform the vibrational integration. The numerical results for $\lambda'(R)$ were fitted to a quadratic polynomial[38]

$$\lambda'(\xi) = \lambda'_e + \lambda'_1\xi + \lambda'_2\xi^2\,, \qquad (8)$$

where $\xi=(R-R_e)/R_e$ and the fourth power of the vibrational wave function was used as a weighting factor.

The vibrationally averaged result of −0.04089 cm^{-1}, given in Table IV, agrees with the experimental value[1] of −0.0367 cm^{-1}, to within 11%. Such agreement does not occur often.

Due to centrifugal stretching,[39] the two rotational levels measured ($K=1$ and $K=3$)[1] have slightly different $\lambda'(K)$ corresponding to the slightly different equilibrium distances. Denoting the quantity

$$(R_e/\bar{\lambda}')(d\bar{\lambda}'/dR_e)$$

by a, one experimentally[1] obtains $a=-2.5$. On the other hand the change in $\lambda'(R)$ compared to the change in R at $R=R_e$ is given by

$$(R_e/\lambda')(d\lambda'/dR)_{R=R_e}\,,$$

and this quantity, which is essentially a, is computed to be −4.71.

The fine-structure constant was rather sensitive to the addition of various wave functions, suggesting that further improvement would involve enlargement of the number of configurations and/or the basis set. The stability of $\lambda'_1\xi$ [Eq. (8)] seems to indicate the need for more configurations, rather than improvement of the basis set.

TABLE III. Values of $\lambda'(R)$ as a function of R. The experimental equilibrium distance is 1.981 a.u.

R (in a.u.)	$\lambda'(R)$ (in cm^{-1})
1.800	−0.057 29
1.900	−0.046 44
2.015	−0.035 25
2.130	−0.025 52
2.245	−0.017 30

II. SECOND-ORDER SPIN-ORBIT CONTRIBUTION TO λ

For Σ states, the first-order spin-orbit energy is zero, and the second-order energy is given by

$$\tfrac{2}{3}\lambda''(R)[3\Sigma^2-S(S+1)]. \tag{9}$$

The only states interacting, through the spin-orbit operator, with $a\,^3\Sigma_u^+$ are $^{1,3,5}\Pi_u$ and $^{1,3,5}\Sigma_u^-$ as Kayama and Baird have shown.[3] This is true for the full spin-orbit operator, which includes all two-particle contributions, as well as modifications thereof. The molecular-orbital (MO) configuration which dominates the $a\,^3\Sigma_u^+$ state is $1\sigma_g^2 1\sigma_u 2\sigma_g$, and it can be seen that both the quintets, involving four singly occupied molecular orbitals and the $^{1,3}\Sigma_u^-$ states, such as $1\sigma_g^2 1\pi_u 1\pi_g$ are too highly excited to contribute significantly. This is distinguished from O_2, where the dominant configuration can produce both a singlet Σ^+ and a triplet Σ^- state. The remaining $^{1,3}\Pi_u$ states arise from configurations such as $1\sigma_g^2 1\sigma_u nd\pi$.[39] It is well known, however, that the major part of the full spin-orbit operator can be written as $\sum_{i=1}^{N} A_i(r_i)\vec{l}_i\cdot\vec{s}_i$. The residual two-particle part is only significant when the reduced one-particle contribution is very small. An example of this occurs in $\sigma\pi^{2}\,{}^2\Delta$ states.[40] The two-center contributions to the reduced one-particle spin-orbit operator have been shown by Walker and Richards to be negligible in most cases.[19] Since $2\sigma_g$ has predominantly s symmetry, and $nd\pi$ has predominantly d symmetry, the one-center contribution must be very small. The spin-orbit coupling of $1\sigma_g^2 1\sigma_u 2\sigma_g$ $a\,^3\Sigma_u^+$ and $1\sigma_g^2 1\sigma_u nd\pi$ $^{1,3}\Pi_u$ is therefore negligible. As argument based on either the separated-atom[1] or united-atom fine-structure splittings produces the same conclusion.

III. SPIN-ROTATION CONTRIBUTION TO THE FINE STRUCTURE

Phenomenologically, the spin-rotation operator is given by

$$H_{\mathrm{SR}}=\mu\vec{K}\cdot\vec{S}, \tag{10}$$

and hence any microscopic operators having matrix elements proportional to $\vec{K}\cdot\vec{S}$ contribute to the spin-rotational constant μ. The first-order operator is

$$H_{\mathrm{SR}}^{(1)}=-\frac{g\beta}{c}\sum_{K,j}\frac{Z_K e}{r_{jK}^3}[\vec{r}_{jK}\times\vec{V}_K]\cdot\vec{s}_j\,, \tag{11}$$

which has been reduced by Tinkham and Strandberg, for Σ states of homonuclear diatomic molecules to[6(a)]

$$H_{\mathrm{SR}}^{(1)}=\frac{4g\beta\beta_N}{R}\left(\frac{M_P}{A}\right)Z\sum_j\frac{z_{aj}}{r_{aj}^3}\vec{K}\cdot\vec{s}_j\,, \tag{12}$$

where β, β_N are the electron and nuclear magnetons, g is the electronic g factor, A/M_p is the dimensionless atomic mass, and r_{aj} is the vector from the ath nucleus to the jth electron with an internuclear component of z_{aj}. Since $K_z=0$, $H_{\mathrm{SR}}^{(1)}$ will only connect electronic states which differ in Σ by ±1.

TABLE IV. Vibrationally averaged first-order spin-spin constant $\bar{\lambda}'$ and parameters of the least-squares-fit parameters (in cm^{-1}). $\lambda'(\xi)$ is fit to Eq. (8).

Quantity	Theory	Experiment[a]
λ'_e	−0.039 93	
$\lambda'_1\xi$	+0.1881ξ	
$\lambda'_2\xi^2$	−0.2237ξ^2	
$\bar{\lambda}'_1$	−0.040 89	
λ		−0.0367

[a] Reference 1.

The second-order spin-rotation constant μ'' arises from the product of matrix elements between the full spin-orbit operator H_{so} and the orbital-rotation operator H_{or}.[3] For the $a\,^3\Sigma_u^+$ state, only $^3\Pi_u$ states will contribute significantly to μ''. Frequently it is found that μ'' is at least as large as μ'. *Ab initio* evaluation of μ'' is difficult.[41]

For the $a\,^3\Sigma_u^+$ state of He_2, μ'' is expected to be considerably smaller than normal due to the small size of the spin-orbit coupling and because the orbital-rotation operator will have a small one-center part. Lichten *et al.*[1] however, have estimated μ' to have an order of magnitude of +5 MHz; while the measured value of μ is −2.5 MHz, suggesting that $|\mu''|>|\mu'|$.

Although μ makes a small contribution to the fine structure (5 out of 1000 MHz), the experimental precision is such that it can be obtained. The high-frequency nuclear shielding constant σ^{HF} is related to μ'' as Ramsey has shown.[41] We are calculating μ' and from this we will be able to obtain μ'' semiempirically by subtraction.

Further contributions to the fine structure arising from the perturbation of the rotational levels by the fine-structure operators[13] are small since λ_e/B_e for this state is approximately 5×10^{-3}.

IV. COMPARISON OF THE FINE-STRUCTURE SEPARATIONS

The fine-structure separations are given by

$$W_{K,J=K}-W_{K,J=K-1}=\frac{2\lambda' K}{2K-1}\,,$$

$$W_{K,J=K+1}-W_{K,J=K}=-2\,\frac{\bar{\lambda}'(K+1)}{(2K+3)}\,. \tag{13}$$

TABLE V. Fine-structure separations for the $K=1$ and 3 rotational levels of the $a\,^3\Sigma_u^+$ state of He_2 (in GHz). The chief source of disagreement is due to the differing values of the spin-spin constant (Table IV).

K	J'	J	$W_{K,J'}-W_{K,J}$ Theory	Experiment[a]
1	1	0	−2.451	−2.199 968
1	2	1	+0.9806	+0.873 668
3	3	2	−1.471	−1.323 911
3	4	3	+1.091	+0.964 992

[a] Reference 1.

These are just Kramers formulas[42] when the spin-rotation constant and the K dependence of $\bar{\lambda}'$ are neglected. Our results for the fine-structure separations are given in Table V. The agreement with experiment is good.

V. CONCLUSIONS

We have calculated the first-order spin-spin coupling constant for the $a\,^3\Sigma_u^+$ state of He_2. This *ab initio* calculation has firmly established the sign of the constant.[2] While the wave function employed here does not give a particularly good dissociation energy, yielding 0.94 eV instead of 1.76 eV,[12(a)] the spin-spin constant agrees with experiment to 11%. The hybrid integrals are found to make a significant contribution to λ'.

Our results show that it is consistent to neglect second-order spin-orbit coupling, the spin-rotation coupling constant, and the corrections of Schlapp.[13]

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