PHYSICAL REVIEW A, VOLUME 61, 042705

Calculation of properties of two-center systems

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(Received 5 August 1999; published 6 March 2000)

A procedure is described by which the response of a two-center system to a perturbation can be expressed in terms of single-center wave functions. We use the formulation to evaluate the asymptotic long-range part of the Pauli-Dirac relativistic interaction between two ground-state hydrogen atoms and compare with the results of *ab initio* calculations.

PACS number(s): 34.20.Cf

I. INTRODUCTION

The study of atomic collisions in ultracold regimes has become important in interpreting observations made possible by the current experimental techniques for cooling and trapping gaseous atomic samples; topics attracting interest include the construction of gaseous Bose-Einstein condensates, accurate measurement of time, and the production of molecules in specified vibrational states by cold atom photoassociation. Reviews of ultracold atomic physics are given in [1].

This current interest in cold atomic collisions brings a need for precise interaction potentials because the effects on scattering induced by small corrections to the potentials are enhanced at the very low energies of the ultracold ensembles.

Relativistic corrections influence the scattering at ultralow temperatures. They have been calculated for the $X\,^1\Sigma_g^+$ state of H_2 by *ab initio* variational methods for internuclear distances R between 0 bohr and 12 bohr [2] but their asymptotic form has not been determined. We introduce here a procedure with which a precise determination can be achieved. We extend the calculations of Wolniewicz [2] to larger values of R for both the $X\,^1\Sigma_g^+$ and $b\,^3\Sigma_u^+$ states and compare the results with the calculated long-range form.

The procedure, in which the effects of certain two-center interactions are factored into products of one-center functions, is general and we describe it in Secs. II and III. We apply it to the relativistic interaction calculation in Sec. IV and present the *ab initio* calculations in Sec. V.

II. TWO-CENTER PERTURBATION

We consider an unperturbed two-center dynamical system consisting of a particle labeled 1 centered on point **A** and moving in the potential $V_{\mathrm{a}}(\mathbf{r}_1^{\mathrm{a}})=V_{\mathrm{a}}(r_1^{\mathrm{a}})$ where $\mathbf{r}_1^{\mathrm{a}}$ is its displacement from **A** and a particle labeled 2 centered on point **B** and moving in the potential $V_{\mathrm{b}}(\mathbf{r}_2^{\mathrm{b}})=V_{\mathrm{b}}(r_2^{\mathrm{b}})$ where $\mathbf{r}_2^{\mathrm{b}}$ is its displacement from **B**. The wave function $\psi_0(\mathbf{r}_1^{\mathrm{a}},\mathbf{r}_2^{\mathrm{b}})$ of the system satisfies the equation

$$(H_0-E_0)\,\psi_0(\mathbf{r}_1^{\mathrm{a}},\mathbf{r}_2^{\mathrm{b}})=0 \tag{1}$$

where H_0 and E_0 are the unperturbed Hamiltonian and energy, respectively, given by the sum of the separate Hamiltonians or energies for the centers **A** and **B**. The Hamiltonian for center **A** is

$$H_0^{\mathrm{a}}=-\frac{\hbar^2}{2m_1}\nabla^2_{1\mathrm{a}}+V_{\mathrm{a}}(r_1^{\mathrm{a}}) \tag{2}$$

where m_1 is the mass of particle 1, and the Hamiltonian H_0^{b} for center **B** is defined similarly. We may write the wave function as the product

$$\psi_0(\mathbf{r}_1^{\mathrm{a}},\mathbf{r}_2^{\mathrm{b}})=u_{\mathrm{a}}(\mathbf{r}_1^{\mathrm{a}})u_{\mathrm{b}}(\mathbf{r}_2^{\mathrm{a}}) \tag{3}$$

where $u_{\mathrm{a}}(\mathbf{r}_1^{\mathrm{a}})$, assumed to be normalized, satisfies the equation

$$(H_0^{\mathrm{a}}-E_0^{\mathrm{a}})u_{\mathrm{a}}(\mathbf{r}_1^{\mathrm{a}})=0 \tag{4}$$

and $u_{\mathrm{b}}(\mathbf{r}_2^{\mathrm{b}})$ satisfies a similar equation. We introduce the two-center perturbation

$$V(\mathbf{r}_1^{\mathrm{a}},\mathbf{r}_2^{\mathrm{b}})=\sum_{i=1}^{N} f_{\mathrm{a}}^{(i)}(\mathbf{r}_1^{\mathrm{a}})f_{\mathrm{b}}^{(i)}(\mathbf{r}_2^{\mathrm{b}}). \tag{5}$$

Let

$$\mathcal{P}=\mathcal{I}-|\psi_0\rangle\langle\psi_0| \tag{6}$$

be the operator that projects off the unperturbed state $|\psi_0\rangle$, assumed normalized, where $\mathcal{I}$ denotes the identity operator. The first-order wave function $\psi_1(\mathbf{r}_1^{\mathrm{a}},\mathbf{r}_2^{\mathrm{b}})$, chosen to be orthogonal to the unperturbed wave function, satisfies the equation

$$|\psi_1\rangle=-\mathcal{P}(H_0-E_0)^{-1}\mathcal{P}V|\psi_0\rangle=-(H_0-E_0)^{-1}\mathcal{P}V|\psi_0\rangle. \tag{7}$$

The second-order wave function satisfies the equation

$$\begin{aligned}|\psi_2\rangle={}&\mathcal{P}(H_0-E_0)^{-1}\mathcal{P}(V-\langle\psi_0|V|\psi_0\rangle)\\&\times\mathcal{P}(H_0-E_0)^{-1}\mathcal{P}V|\psi_0\rangle\end{aligned} \tag{8}$$

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which, if $\langle\psi_0|V|\psi_0\rangle$ vanishes through, for example, symmetry considerations, may be written

$$|\psi_2\rangle=(H_0-E_0)^{-1}\mathcal{P}V(H_0-E_0)^{-1}\mathcal{P}V|\psi_0\rangle. \tag{9}$$

Let $\mathcal{P}_\mathrm{a}$ and $\mathcal{P}_\mathrm{b}$ project out the ground states, assumed normalized, of the single-center Hamiltonians H_0^a and H_0^b, respectively. Then

$$\mathcal{P}=\mathcal{P}_\mathrm{a}|u_\mathrm{b}\rangle\langle u_\mathrm{b}|+\mathcal{P}_\mathrm{b}|u_\mathrm{a}\rangle\langle u_\mathrm{a}|+\mathcal{P}_\mathrm{a}\mathcal{P}_\mathrm{b}. \tag{10}$$

We need

$$(H_0-E_0)^{-1}=[(H_0^\mathrm{a}-E_0^\mathrm{a})+(H_0^\mathrm{b}-E_0^\mathrm{b})]^{-1} \tag{11}$$

which we may rewrite using the integral, for a and b positive,

$$(a+b)^{-1}=\frac{2}{\pi}\int_0^\infty d\omega\,\frac{ab}{(a^2+\omega^2)(b^2+\omega^2)}. \tag{12}$$

Equation (12) enables us to obtain a product form for the first-order wave function, albeit with the need to evaluate an integral. We use Eqs. (3), (5), (7), (10), (11), and (12) to express the first-order wave function as the following sum of single-center products:

$$\begin{aligned}\psi_1(\mathbf{r}_1^\mathrm{a},\mathbf{r}_2^\mathrm{b})=&-\sum_{i=1}^{N}\frac{1}{H_0^\mathrm{a}-E_0^\mathrm{a}}\mathcal{P}_\mathrm{a}f_\mathrm{a}^{(i)}(\mathbf{r}_1^\mathrm{a})u_\mathrm{a}(\mathbf{r}_1^\mathrm{a})\langle u_\mathrm{b}|f_\mathrm{b}^{(i)}|u_\mathrm{b}\rangle u_\mathrm{b}(\mathbf{r}_2^\mathrm{b})\\&-\sum_{i=1}^{N}\frac{1}{H_0^\mathrm{b}-E_0^\mathrm{b}}\mathcal{P}_\mathrm{b}f_\mathrm{b}^{(i)}(\mathbf{r}_2^\mathrm{b})u_\mathrm{b}(\mathbf{r}_2^\mathrm{b})\langle u_\mathrm{a}|f_\mathrm{a}^{(i)}|u_\mathrm{a}\rangle u_\mathrm{a}(\mathbf{r}_1^\mathrm{a})\\&-\frac{2}{\pi}\sum_{i=1}^{N}\int_0^\infty d\omega\,\frac{H_0^\mathrm{a}-E_0^\mathrm{a}}{(H_0^\mathrm{a}-E_0^\mathrm{a})^2+\omega^2}\mathcal{P}_\mathrm{a}f_\mathrm{a}^{(i)}(\mathbf{r}_1^\mathrm{a})\\&\times u_\mathrm{a}(\mathbf{r}_1^\mathrm{a})\frac{H_0^\mathrm{b}-E_0^\mathrm{b}}{(H_0^\mathrm{b}-E_0^\mathrm{b})^2+\omega^2}\mathcal{P}_\mathrm{b}f_\mathrm{b}^{(i)}(\mathbf{r}_2^\mathrm{b})u_\mathrm{b}(\mathbf{r}_2^\mathrm{b}).\end{aligned} \tag{13}$$

The first term in Eq. (13) may be obtained from the solution $\theta_\mathrm{a}^{(i)}(\mathbf{r}_1^\mathrm{a})$ of the equation

$$(H_0^\mathrm{a}-E_0^\mathrm{a})\,\theta_\mathrm{a}^{(i)}(\mathbf{r}_1^\mathrm{a})=\mathcal{P}_\mathrm{a}f_\mathrm{a}^{(i)}(\mathbf{r}_1^\mathrm{a})u_\mathrm{a}(\mathbf{r}_1^\mathrm{a}) \tag{14}$$

and the second term may be found similarly. In studies of interacting atoms that have no permanent dipole or higher moments these *induction* terms vanish identically. The last term in Eq. (13) is

$$\psi_1(\mathbf{r}_1^\mathrm{a},\mathbf{r}_2^\mathrm{b})=-\frac{2}{\pi}\sum_{i=1}^{N}\int_0^\infty d\omega\,\chi_\mathrm{a}^{(i)}(\omega;\mathbf{r}_1^\mathrm{a})\chi_\mathrm{b}^{(i)}(\omega;\mathbf{r}_2^\mathrm{b}) \tag{15}$$

where $\chi_\mathrm{a}^{(i)}(\omega;\mathbf{r}_1^\mathrm{a})$ satisfies the equation

$$\begin{aligned}[(H_0^\mathrm{a}-E_0^\mathrm{a})^2+\omega^2]\chi_\mathrm{a}^{(i)}(\omega;\mathbf{r}_1^\mathrm{a})=&(H_0^\mathrm{a}-E_0^\mathrm{a})\mathcal{P}_\mathrm{a}f_\mathrm{a}^{(i)}(\mathbf{r}_1^\mathrm{a})u_\mathrm{a}(\mathbf{r}_1^\mathrm{a})\\&+\omega^2\langle u_\mathrm{a}|\chi_\mathrm{a}^{(i)}\rangle u_\mathrm{a}(\mathbf{r}_1^\mathrm{a})\end{aligned} \tag{16}$$

and $\chi_\mathrm{b}^{(i)}(\omega;\mathbf{r}_2^\mathrm{b})$ satisfies a similar equation. Equation (16) may be solved by direct numerical methods [3] or by variational methods such as that used by Chan and Dalgarno [4], who calculated the dynamical polarizability of atomic hydrogen by finding the stationary values of the functional

$$\begin{aligned}J_\mathrm{a}^{(i)}(\omega)=&\langle\Xi_\mathrm{a}^{(i)}|(H_0^\mathrm{a}-E_0^\mathrm{a})^2+\omega^2|\Xi_\mathrm{a}^{(i)}\rangle\\&-2\langle\Xi_\mathrm{a}^{(i)}|H_0^\mathrm{a}-E_0^\mathrm{a}|u_\mathrm{a}\rangle-\omega^2|\langle\Xi_\mathrm{a}^{(i)}|u_\mathrm{a}\rangle|^2\end{aligned} \tag{17}$$

with respect to a trial function $\Xi_\mathrm{a}^{(i)}(\omega;\mathbf{r}_1^\mathrm{a})$. We adopt their method.

III. PERTURBED EXPECTATION VALUE

Suppose we wish to determine the expectation value of the operator $L=L_\mathrm{a}+L_\mathrm{b}$, effective on each center separately, in the presence of the two-center perturbation (5). The zeroth-order contribution is straightforward to evaluate.

The first-order contribution is (with $\langle\psi_0|\psi_1\rangle$ vanishing)

$$L_1=\langle\psi_0|L|\psi_1\rangle+\langle\psi_1|L|\psi_0\rangle \tag{18}$$

which may be expressed with the aid of Eqs. (13) and (15) as

$$\begin{aligned}L_1=-\frac{2}{\pi}\sum_{i=1}^{N}\int_0^\infty d\omega(&\langle u_\mathrm{a}|L_\mathrm{a}|\chi_\mathrm{a}^{(i)}\rangle\langle u_\mathrm{b}|\chi_\mathrm{b}^{(i)}\rangle\\&+\langle u_\mathrm{b}|L_\mathrm{b}|\chi_\mathrm{b}^{(i)}\rangle\langle u_\mathrm{a}|\chi_\mathrm{a}^{(i)}\rangle+\langle\chi_\mathrm{a}^{(i)}|L_\mathrm{a}|u_\mathrm{a}\rangle\langle\chi_\mathrm{b}^{(i)}|u_\mathrm{b}\rangle\\&+\langle\chi_\mathrm{b}^{(i)}|L_\mathrm{b}|u_\mathrm{b}\rangle\langle\chi_\mathrm{a}^{(i)}|u_\mathrm{a}\rangle).\end{aligned} \tag{19}$$

The second-order contribution is (with $\langle\psi_0|\psi_2\rangle$ vanishing)

$$\begin{aligned}L_2=&\langle\psi_1|L|\psi_1\rangle+\langle\psi_0|L|\psi_2\rangle+\langle\psi_2|L|\psi_0\rangle\\&-\langle\psi_0|L|\psi_0\rangle\langle\psi_1|\psi_1\rangle.\end{aligned} \tag{20}$$

It is not necessary to find the second-order wave function to evaluate L_2; we can use the first-order wave function and another first-order wave function corresponding to the perturbation L to evaluate the matrix elements $\langle\psi_0|L|\psi_2\rangle$ and $\langle\psi_2|L|\psi_0\rangle$ [5]. From Eqs. (7) and (9) we may write (with $\langle\psi_0|V|\psi_0\rangle$ vanishing)

$$\langle\psi_0|L|\psi_2\rangle=-\langle\psi_0|L(H_0-E_0)^{-1}\mathcal{P}V|\psi_1\rangle=\langle\phi_1|V|\psi_1\rangle \tag{21}$$

where $|\phi_1\rangle$ is the first-order wave function induced by the perturbation L *alone*, chosen orthogonal to $|\psi_0\rangle$, that satisfies the equation

$$(H_0-E_0)|\phi_1\rangle+(L-\langle\psi_0|L|\psi_0\rangle)|\psi_0\rangle=0. \tag{22}$$

Similarly we find

$$\langle \psi_2 | L | \psi_0 \rangle = \langle \psi_1 | V | \phi_1 \rangle. \tag{23}$$

We may express ϕ_1 as

$$\phi_1(\mathbf{r}_1^{\mathrm{a}}, \mathbf{r}_2^{\mathrm{b}}) = [g_{\mathrm{a}}(\mathbf{r}_1^{\mathrm{a}}) + g_{\mathrm{b}}(\mathbf{r}_2^{\mathrm{b}})] \psi_0(\mathbf{r}_1^{\mathrm{a}}, \mathbf{r}_2^{\mathrm{b}}) \tag{24}$$

where $g_{\mathrm{a}}(\mathbf{r}_1^{\mathrm{a}})$ satisfies the equation

$$(H_0^{\mathrm{a}} - E_0^{\mathrm{a}}) g_{\mathrm{a}}(\mathbf{r}_1^{\mathrm{a}}) u_{\mathrm{a}}(\mathbf{r}_1^{\mathrm{a}}) + (L_{\mathrm{a}} - \langle u_{\mathrm{a}} | L_{\mathrm{a}} | u_{\mathrm{a}} \rangle) u_{\mathrm{a}}(\mathbf{r}_1^{\mathrm{a}}) = 0 \tag{25}$$

[6] and $g_{\mathrm{b}}(\mathbf{r}_2^{\mathrm{b}})$ satisfies a similar equation. From Eqs. (15), (20), (21), (23), and (24) we obtain

$$\begin{aligned} L_2 = {} & \frac{4}{\pi^2} \sum_{i=1}^{N} \sum_{j=1}^{N} \int_0^\infty d\omega \, d\omega' [\langle \chi_{\mathrm{a}}^{(i)}(\omega) | L_{\mathrm{a}} | \chi_{\mathrm{a}}^{(j)}(\omega') \rangle \langle \chi_{\mathrm{b}}^{(i)}(\omega) | \chi_{\mathrm{b}}^{(j)}(\omega') \rangle + \langle \chi_{\mathrm{b}}^{(i)}(\omega) | L_{\mathrm{b}} | \chi_{\mathrm{b}}^{(j)}(\omega') \rangle \langle \chi_{\mathrm{a}}^{(i)}(\omega) | \chi_{\mathrm{a}}^{(j)}(\omega') \rangle] \\ & + \frac{2}{\pi} \sum_{i=1}^{N} \sum_{j=1}^{N} \int_0^\infty d\omega [\langle g_{\mathrm{a}} u_{\mathrm{a}} | f_{\mathrm{a}}^{(j)} | \chi_{\mathrm{a}}^{(i)}(\omega) \rangle \langle u_{\mathrm{b}} | \chi_{\mathrm{b}}^{(i)}(\omega) \rangle + \langle g_{\mathrm{b}} u_{\mathrm{b}} | f_{\mathrm{b}}^{(j)} | \chi_{\mathrm{b}}^{(i)}(\omega) \rangle \langle u_{\mathrm{a}} | \chi_{\mathrm{a}}^{(i)}(\omega) \rangle + \langle \chi_{\mathrm{a}}^{(i)}(\omega) | f_{\mathrm{a}}^{(j)} | g_{\mathrm{a}} u_{\mathrm{a}} \rangle \\ & \times \langle \chi_{\mathrm{b}}^{(i)}(\omega) | u_{\mathrm{b}} \rangle + \langle \chi_{\mathrm{b}}^{(i)}(\omega) | f_{\mathrm{b}}^{(j)} | g_{\mathrm{b}} u_{\mathrm{b}} \rangle \langle \chi_{\mathrm{a}}^{(i)}(\omega) | u_{\mathrm{a}} \rangle] - \frac{4}{\pi^2} (\langle u_{\mathrm{a}} | L_{\mathrm{a}} | u_{\mathrm{a}} \rangle + \langle u_{\mathrm{b}} | L_{\mathrm{b}} | u_{\mathrm{b}} \rangle) \sum_{i=1}^{N} \int_0^\infty d\omega \langle \chi_{\mathrm{a}}^{(i)}(\omega) | \chi_{\mathrm{a}}^{(i)}(\omega) \rangle \\ & \times \sum_{i=1}^{N} \int_0^\infty d\omega \langle \chi_{\mathrm{b}}^{(i)}(\omega) | \chi_{\mathrm{b}}^{(i)}(\omega) \rangle. \end{aligned} \tag{26}$$

IV. APPLICATION TO LONG-RANGE PROPERTIES

The method described in Secs. II and III is generally applicable to two-center problems. We need to be able to solve equations of the form (25); the method is much more convenient when this equation has an analytic solution. The Dirac contribution is an important part of the relativistic energy of two interacting ground-state hydrogen atoms and influences cold collisions and it happens that its calculation provides an example where Eq. (25) can be solved analytically, as we demonstrate below.

In the Pauli approximation the Dirac energy of the hydrogen molecule is [2,7]

$$\epsilon_4 = \pi \alpha^2 e^2 a_0^2 [\delta^{(3)}(\mathbf{r}_1^{\mathrm{a}}) + \delta^{(3)}(\mathbf{r}_2^{\mathrm{b}}) - \delta^{(3)}(\mathbf{r}_1^{\mathrm{a}} - \mathbf{r}_2^{\mathrm{b}} - \mathbf{R})] \tag{27}$$

where α is the fine structure constant, e is the electronic charge, a_0 denotes one bohr, and $\delta^{(3)}$ is the three-dimensional delta function. The δ function has dimension $[L]^{-3}$. The third term vanishes for the triplet state and decreases exponentially for the singlet state. The leading two terms decrease as inverse powers of R. To evaluate the long-range perturbation of the expectation value of the δ function we identify the operator L with $\delta^{(3)}(\mathbf{r}_1^{\mathrm{a}}) + \delta^{(3)}(\mathbf{r}_2^{\mathrm{b}})$ and the perturbation $V(\mathbf{r}_1^{\mathrm{a}}, \mathbf{r}_2^{\mathrm{b}})$ with the long-range electrostatic interaction between the atoms. The dipole-dipole component of this interaction can be expressed as a sum of one-center products such as Eq. (5) by [8]

$$V(\mathbf{r}_1^{\mathrm{a}}, \mathbf{r}_2^{\mathrm{b}}) = -\frac{4\pi e^2}{3R^3} \sum_{\alpha=-1}^{1} C_{1+\alpha}^{2} \mathcal{Y}_{1,\alpha}(\mathbf{r}_1^{\mathrm{a}}) \mathcal{Y}_{1,-\alpha}(\mathbf{r}_2^{\mathrm{b}}) \tag{28}$$

where C_m^n denotes the binomial coefficient and $\mathcal{Y}_{1,\alpha}(\mathbf{r}) = r Y_{1,\alpha}(\hat{\mathbf{r}})$.

The Hamiltonians H_0^{a} and H_0^{b}, the perturbations f_{a} and f_{b}, and the operators L_{a} and L_{b} do not depend essentially on the centers; henceforth where possible we dispense with notation that distinguishes the centers.

The normalized ground-state orbital is

$$u(\mathbf{r}) = u_{1s}(r) Y_{0,0}(\hat{\mathbf{r}}) = 2 \exp(-r) Y_{0,0}(\hat{\mathbf{r}}). \tag{29}$$

The expectation value of the δ function summed over *both* centers to zeroth order is $2a_0^{-3}\pi^{-1}$, or $2\pi^{-1}$ in atomic units.

From $\nabla^2 r^{-1} = -4\pi\delta^{(3)}(\mathbf{r})$ Dalgarno and Stewart [9] found a closed form expression for $g(\mathbf{r})$; with our requirement that $\phi(\mathbf{r})$ and $u(\mathbf{r})$ are orthogonal it is (in atomic units)

$$g(\mathbf{r}) = g(r) = \frac{1}{2\pi} [-r^{-1} + 2 \ln r + 2r - \overline{\tfrac{1}{2} + 2\Psi(3) - 2 \ln 2}] \tag{30}$$

where $\Psi(k)$ is the digamma function (see the Appendix). We note that $\Psi(3) \approx 0.922\,784\,335\,1$ and $\ln 2 \approx 0.693\,147\,180\,6$. The overlined terms ensure orthogonality. The dimensions of $g(\mathbf{r})$ are $[E]^{-1}[L]^{-1}$.

For any given value of ω Eq. (16) can be solved variationally by adopting the trial function

$$\Xi^{(\alpha)}(\omega; \mathbf{r}) = F(\omega; r) Y_{1,\alpha}(\hat{\mathbf{r}}) u(\mathbf{r}) = \sum_{p=1}^{n} a_p(\omega) r^p Y_{1,\alpha}(\hat{\mathbf{r}}) u(\mathbf{r}) \tag{31}$$

and finding the stationary values of the functional (17) with respect to variations in the coefficients $a_p(\omega)$. The dimensions of $F(\omega;r)$ are $[E]^{-1/2}[L]^{-3/2}$. The coefficients satisfy a matrix equation whose elements, being combinations of expectation values of powers of r for the ground-state hydrogen wave function, can be found following (considerable) algebraic manipulation; Chan [10] has presented the matrix equations. The first-order contribution to the expectation value of the δ function vanishes on account of angular symmetry. The trial function determined as described above can be substituted into Eq. (26) and the necessary quadratures over ω performed to yield the second-order contribution, whose R dependence is R^{-6}. The perturbed wave functions are each linear in r *near* each center and hence the δ functions in the first term of L_2 in Eq. (26) cause that term to vanish.

The second and third parts of L_2 involve the sum of integrals

$$I=\sum_{\alpha=-1}^{1}\sum_{\beta=-1}^{1}C_{1+\alpha}^2C_{1+\beta}^2\int\int d\hat{\mathbf{r}}_1d\hat{\mathbf{r}}_2Y_{1,\alpha}^*(\hat{\mathbf{r}}_1)Y_{0,0}^*(\hat{\mathbf{r}}_1)\times Y_{1,\beta}(\hat{\mathbf{r}}_1)Y_{0,0}(\hat{\mathbf{r}}_1)Y_{1,-\alpha}^*(\hat{\mathbf{r}}_2)Y_{0,0}^*(\hat{\mathbf{r}}_2)Y_{1,-\beta}(\hat{\mathbf{r}}_2)Y_{0,0}(\hat{\mathbf{r}}_2). \tag{32}$$

The integration over $\hat{\mathbf{r}}_1$ yields a factor

$$I_1=-\frac{3}{4\pi}\begin{pmatrix}1&1&0\\0&0&0\end{pmatrix}\begin{pmatrix}1&1&0\\-\alpha&\beta&0\end{pmatrix}=-\frac{1}{4\pi}\delta_{\alpha,-\beta} \tag{33}$$

and hence

$$I=\frac{1}{16\pi^2}\sum_{\alpha=-1}^{1}C_{1+\alpha}^2C_{1-\alpha}^2=\frac{1}{16\pi^2}C_2^4=\frac{3}{8\pi^2}. \tag{34}$$

The second part of L_2 in Eq. (26) becomes

$$-\frac{16a_0^3}{3\pi R^6}\int_0^\infty d\omega\int_0^\infty r^2drF(\omega;r)g(r)ru_{1s}(r)\times\int_0^\infty r^2drF(\omega;r)ru_{1s}(r). \tag{35}$$

The third part of L_2 in Eq. (26) is

$$-\frac{16a_0^3}{3\pi^3R^6}\int_0^\infty\int_0^\infty\int_0^\infty d\omega\, d\omega' r^2drF(\omega;r)F(\omega';r)u_{1s}(r). \tag{36}$$

The total second-order contribution is obtained by adding the expressions (35) and (36). Once the coefficients $a_p(\omega)$ are known for a value of ω the quadratures over r in expressions (35) and (36) can be done analytically. We performed the quadratures over ω over the range [0,100] by Simpson's rule and added the contributions from the range [100,∞] which was evaluated analytically using the asymptotic form for the perturbed wave functions; Eq. (16) shows that the dependence is as ω^{-2} for large values of ω. Six terms proved sufficient in the trial function to achieve convergence. The intermediate numerical data that Chan and Dalgarno included because of their possible future utility were used in a check of our presently adopted numerical procedures.

TABLE I. Born-Oppenheimer potentials (hartree).

R (bohr)	$X\,^1\Sigma_g^+$	$b\,^3\Sigma_u^+$
1.0	−1.124539713	−0.622264306
1.5	−1.172855073	−0.809666437
2.0	−1.138132950	−0.897076283
2.5	−1.093938123	−0.945453719
3.0	−1.057326262	−0.972015035
3.5	−1.031858079	−0.986130885
4.0	−1.016390249	−0.993380059
4.5	−1.007993726	−0.996972880
5.0	−1.003785656	−0.998687253
5.5	−1.001774578	−0.999471748
6.0	−1.000835707	−0.999813447
6.5	−1.000400548	−0.999952833
7.0	−1.000197914	−1.000003987
7.5	−1.000102106	−1.000018912
8.0	−1.000055605	−1.000020214
8.5	−1.000032172	−1.000017232
9.0	−1.000019782	−1.000013517
9.5	−1.000012856	−1.000010246
10.0	−1.000008755	−1.000007674
10.5	−1.000006190	−1.000005744
11.0	−1.000004506	−1.000004323
11.5	−1.000003356	−1.000003281
12.0	−1.000002546	−1.000002515
12.5	−1.000001961	−1.000001948
13.0	−1.000001529	−1.000001524
13.5	−1.000001206	−1.000001204
14.0	−1.000000961	−1.000000960
14.5	−1.000000772	−1.000000772
15.0	−1.000000625	−1.000000625
15.5	−1.000000510	−1.000000510
16.0	−1.000000420	−1.000000420
16.5	−1.000000347	−1.000000347
17.0	−1.000000289	−1.000000289
17.5	−1.000000242	−1.000000242
18.0	−1.000000203	−1.000000203
18.5	−1.000000172	−1.000000172
19.0	−1.000000146	−1.000000146
19.5	−1.000000125	−1.000000125
20.0	−1.000000107	−1.000000107
∞	−1.000000000	−1.000000000

We found that the expectation value of the δ function is perturbed, to $O(R^{-6})$, by $-28.29a_0^3R^{-6}$. Thus asymptotically, in atomic units,

$$\langle\delta^{(3)}(\mathbf{r}_1)+\delta^{(3)}(\mathbf{r}_2)\rangle=\frac{2}{\pi}\left(1-\frac{28.29}{R^6}+\cdots\right). \tag{37}$$

TABLE II. δ function expectation values (bohr^{-3}).

R (bohr)	$X\,^1\Sigma_g^+$	$b\,^3\Sigma_u^+$
1.0	2.023490	1.386921
1.5	1.353334	1.098815
2.0	1.069361	1.073996
2.5	0.948122	1.067863
3.0	0.911053	1.052201
3.5	0.918475	1.035008
4.0	0.942387	1.021268
4.5	0.965166	1.011918
5.0	0.980793	1.006203
5.5	0.989925	1.002990
6.0	0.994839	1.001321
6.5	0.997371	1.000502
7.0	0.998649	1.000101
7.5	0.999293	0.999969
8.0	0.999617	0.999925
8.5	0.999784	0.999930
9.0	0.999871	0.999940
9.5	0.999910	0.999948
10.0	0.999948	0.999960
10.5	0.999965	0.999969
11.0	0.999975	0.999975
11.5	0.999980	0.999980
12.0	0.999984	0.999986
12.5	0.999988	0.999990
13.0	0.999991	0.999992
13.5	0.999993	0.999993
14.0	0.999994	0.999995
14.5	0.999996	0.999997
15.0	0.999996	0.999997
15.5	0.999997	0.999997
16.0	0.999998	0.999998
16.5	0.999999	0.999998
17.0	0.999999	0.999998
17.5	0.999998	0.999999
18.0	0.999998	0.999999
18.5	0.999997	0.999999
19.0	0.999997	0.999999
19.5	0.999997	0.999999
20.0	0.999998	0.999999
∞	1.000000	1.000000

TABLE III. $R^6 L_2$ (bohr^3).

R (bohr)	$X\,^1\Sigma_g^+$	$b\,^3\Sigma_u^+$	Average
8.5	−52	−17	−34
9.0	−43	−20	−31
9.5	−42	−24	−33
10.0	−33	−25	−29
10.5	−30	−26	−28
11.0	−28	−28	−28
11.5	−29	−29	−29
12.0	−30	−27	−29
12.5	−29	−24	−27
13.0	−28	−25	−26
13.5	−27	−27	−27
14.0	−29	−24	−26
14.5	−24	−18	−21
15.0	−29	−22	−25
15.5	−26	−26	−26
16.0	−22	−22	−22
16.5	−13	−26	−20
17.0	−16	−31	−23
17.5	−37	−19	−28
18.0	−44	−22	−33
18.5	−76	−26	−51
19.0	−89	−30	−60
19.5	−104	−35	−70
20.0	−83	−41	−62

V. *AB INITIO* CALCULATIONS

High precision variational methods to calculate Born-Oppenheimer potential energies and eigenfunctions for molecular hydrogen using carefully chosen basis sets have been developed by Kolos and Wolniewicz [11]. Wolniewicz [2] calculated the potential energies of the $X\,^1\Sigma_g^+$ state over the range [0,12] bohr and used the electronic eigenfunctions to calculate the adiabatic and relativistic corrections to the potential energies. We have extended further the calculations of the potential energies and the expectation values of the δ function to a larger range of R and to the $b\,^3\Sigma_u^+$ state. The resulting Born-Oppenheimer energies are given in Table I and the expectation values of $\delta^{(3)}(\mathbf{r}_1)+\delta^{(3)}(\mathbf{r}_2)$ in Table II.

Asymptotically the expectation values of an operator L for the $X\,^1\Sigma_g^+$ and $b\,^3\Sigma_u^+$ states vary as the sum and difference of a direct term L_{dir} that decreases as a series in inverse powers of R and an exchange term L_{exc} which decreases exponentially; at large R

$$L = L_{\mathrm{dir}} \pm L_{\mathrm{exc}}. \tag{38}$$

We have calculated the leading term of L_{dir} for the δ function.

In Table III we show the results of adding the expectation values of the δ function of the $X\,^1\Sigma_g^+$ and $b\,^3\Sigma_u^+$ states for $R \geqslant 8.5$ bohr. The procedure eliminates asymptotically the exchange contribution. Dividing by two and subtracting the zero-order contribution $2/\pi$ yields estimates of the direct term, which tends to $-28.29R^{-6}$ for large R. The values obtained after multiplying by R^6 are given in Table III. The *ab initio* results are less reliable for large R where the chosen basis functions are less appropriate. This is in contrast to the calculated asymptotic results of Sec. IV where the dependence on R is included explicitly. Also the variational calculations are dominated by the zero-order contribution. After it is subtracted we are left with few significant figures. The resulting cancellation error is occasionally large by chance as, for example, at nuclear separations 9.5 bohr, 16.5 bohr, and 18–20 bohr. However, the remaining figures in Table III do serve to show that our evaluation of the asymptotic form, which is numerically exact, is consistent with the *ab initio* results.

VI. CONCLUSION

We have demonstrated how the first-order wave function of a two-center system can be expressed by an integral formula and how it can be used in evaluating the second-order contribution to the expectation values of other operators. We showed that the leading term in the expectation value of the δ function, part of the relativistic interaction between atoms, is proportional to R^{-6} where R is the nuclear separation, and found the calculated coefficient to be consistent with *ab initio* variational calculations for hydrogen atoms at large distances.

ACKNOWLEDGMENTS

This work was done while M.J.J. was visiting the Institute for Theoretical Atomic and Molecular Physics at the Harvard-Smithsonian Center for Astrophysics; he is very pleased to thank the Institute for its hospitality. The Institute is supported by a grant from the National Science Foundation to the Smithsonian Institution and Harvard University. M.J.J. acknowledges support in part for this research from the Engineering and Physical Sciences Research Council. The research of A.D. is supported by the U.S. Department of Energy, Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research.

APPENDIX

To derive the term in Eq. (30) that ensures orthogonality and in performing the quadratures in Eq. (35) we need to evaluate definite integrals of the form $\int_0^\infty dt\,\exp(-st)t^{k-1}\ln t$. We use the equation

$$\int_0^\infty dt\,\exp(-st)\frac{t^{k-1}}{\Gamma(k)}[\Psi(k)-\ln t]=s^{-k}\ln s, \qquad \text{(A1)}$$

from the theory of Laplace transforms [12], where $\Psi(k)$ is the digamma function, which can be calculated from

$$\Psi(k)=1+\frac{1}{2}+\frac{1}{3}+\cdots+\frac{1}{k-1}-\gamma \qquad \text{(A2)}$$

where $\gamma\approx 0.577\,215\,664\,9$ is Euler's constant.

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