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Asymptotic exchange energies for H_2

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An analytical approximation of the asymptotic exchange energy of two interacting hydrogen atoms is obtained. This approximation depends only on functions of the internuclear distance R, which remain bounded as $R \to \infty$ and is derived using the Herring-Holstein surface-integral technique. It is found that, for large R, the exchange energy is $O(R^3 \exp(-2R))$ in contrast to earlier approximations of $O(R^{2.5} \exp(-2R))$. Our result is similar to the classic Heitler-London expression without the unphysical term $O(R^3 \ln(R) \exp(-2R))$.

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I. INTRODUCTION

In a recent paper [1], we examined the problem of the calculation of exchange energies for composite systems with two well-separated nuclei and with a single valence electron. The simplest well-studied case is ${H_2}^+$ at a large value of the internuclear distance R. The other cases treated were alkali-metal ions where most of the electrons were modeled as core atomic systems, and again, we considered one valence orbital. The main aim was to find an approximate analytical formula for the exchange energy in terms of R.

The success of these calculations leads to optimism that the same theoretical structures could be used to deal with situations where the exchange involved two or more electrons. In such cases, it is necessary to invoke the Pauli principle, and in this paper, we perform a preliminary analysis of the problems involved by studying the interaction of two hydrogen atoms (A and B) separated by a large internuclear distance R. The nonrelativistic Schrödinger equation is, in atomic units,

$$H\psi = \left(-\frac{1}{2}\nabla^2 - \frac{1}{r_{1a}} - \frac{1}{r_{1b}} - \frac{1}{r_{2a}} - \frac{1}{r_{2b}} + \frac{1}{r_{12}} + \frac{1}{R}\right)\psi$$
$$= \mathcal{E}\psi, \quad \nabla^2 = \nabla_1^2 + \nabla_2^2. \tag{1}$$

We may write

$$\psi = \phi_a(1)\phi_b(2)f(1,2), \quad E = \mathcal{E} - \frac{1}{R}, \tag{2}$$

where the subscripts a and b denote that these functions are centered on atoms A and B, respectively, and ϕ_a is defined by

$$\left(-\frac{1}{2}\nabla^2 - \frac{1}{r_{1a}} - \frac{1}{r_{1b}}\right)\phi_a = \left(-\frac{1}{2}\nabla_1^2 - \frac{1}{r_{1a}} - \frac{1}{r_{1b}}\right)\phi_a$$
$$= \epsilon_a\phi_a, \tag{3}$$

and, similarly, for ϕ_b for electron 2. From symmetry, $\epsilon_a = \epsilon_b = \epsilon$, and the resulting equation for f is

$$-\frac{1}{2}\nabla^2 f + \frac{1}{r_{12}}f - \boldsymbol{\nabla} f \cdot \frac{\phi_b\nabla_1\phi_a + \phi_a\nabla_2\phi_b}{\phi_a\phi_b} = (E - 2\epsilon)f, \tag{4}$$

where ∇_j is the gradient operator for coordinates j and $\boldsymbol{\nabla} = \nabla_1 + \nabla_2$. This is an exact result, but combinations of the solutions $\psi(1,2)$ and $\psi(2,1)$ are required in order to satisfy the Pauli principle. Here, we consider both the ground-state singlet function with energy E_+, where ψ_+ is symmetric in the interchange of electrons 1 and 2 and the triplet with energy E_- where ψ_- is antisymmetric in the interchange of the two electrons. The usual approximate solution for this problem is obtained variationally, and the classic Heitler-London calculation [2] leads to an asymptotic approximation of the exchange energy given by

$$\tfrac{1}{2}(E_+ - E_-) = -\left(\tfrac{28}{45} - \tfrac{2}{15}[\ln(R) + \gamma]\right) R^3 \exp(-2R)$$
$$+ O(R^2 \exp(-2R))$$
$$= -0.622R^3 \exp(-2R)[1-0.214\,28(\gamma + \ln(R)]$$
$$+ O(R^2 \exp(-2R)), \tag{5}$$

where γ is Euler's constant. This is obtained using a trial function constructed as a product of the two lowest s-state atomic hydrogen wave functions ϕ_a^0,ϕ_b^0 and gives approximations of the states in the form $\psi_\pm = \phi_a^0(1)\phi_b^0(2) \pm \phi_a^0(2)\phi_b^0(1)$. The approximation is physically acceptable for some intervals of R, but eventually, the term in $\ln(R)$ dominates the approximation reversing the sign so that the estimate of the triplet energy is lower than that of the singlet. Here, we construct asymptotic wave functions from a consideration of the large R behavior of the Schrödinger equation and obtain an equation similar to Eq. (5) but without the unphysical term.

II. APPROXIMATIONS FOR LARGE R

We form the approximate wave functions by considering the equations for ϕ_a, ϕ_b, and f as $R \to \infty$. It is convenient to use spheroidal coordinates. With the definition,

$$p_1 = \frac{r_{1a} + r_{1b}}{R}, \quad q_1 = \frac{r_{1a} - r_{1b}}{R}, \quad \phi_a = X(p_1)Y(q_1), \tag{6}$$

Eq. (3) is replaced by the pair of equations,

$$\frac{d}{dp_1}\left\{(p_1^2 - 1)\frac{dX}{dp_1}\right\} + [-C - \lambda^2(p_1^2 - 1) + 2Rp_1]X = 0, \tag{7}$$

$$\frac{d}{dq_1}\left\{(1 - q_1^2)\frac{dY}{dq_1}\right\} + [C - \lambda^2(1 - q_1^2)]Y = 0 \tag{8}$$

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for $1 \leqslant p_1 < \infty$, $-1 \leqslant q_1 \leqslant 1$, where C is the separation constant and

$$\lambda = R\sqrt{\frac{-\epsilon}{2}} = R\alpha. \tag{9}$$

Since we are interested in ground-state calculations, we choose the azimuthal quantum numbers in ϕ_a and ϕ_b to be zero. In Eq. (7), we use $x = 2\lambda(p_1 - 1)$ and write $X = \exp(-x/2)\Phi$ to obtain

$$\begin{aligned} L(\Gamma,1,x)\Phi &= -\eta x L(s,2,x)\Phi, \\ L(a,b,x) &\equiv xD^2 + (b-x)D - a, \end{aligned} \tag{10}$$

$$D = \frac{d}{dx}, \quad \eta = \frac{1}{4\lambda}, \quad \Gamma = \eta C - \frac{1}{2\alpha} + \frac{1}{2}, \quad s = 1 - \frac{1}{\alpha}. \tag{11}$$

This is a form suitable for perturbation theory with parameter η. When η is small, the atoms are well separated, and for $\eta = 0$, we recover one of the separated spheroidal ground-state wave functions for hydrogen. The perturbed wave functions and energies depend on the separation parameter C. In Eq. (8), we perform a similar analysis taking $y = 2\lambda(1 + q_1)$ and $Y = \exp(-y/2)\Theta$, leading to

$$L(\delta,1,y)\Theta = \eta y L(1,2,y)\Theta, \quad D = \frac{d}{dy}, \quad \delta = -\eta C + \frac{1}{2}. \tag{12}$$

In this case, letting $\eta \to 0$ leads to the other spheroidal equation for the isolated atomic hydrogen function centered on atom A. Note that the sign of η differs on the right-hand side of the two perturbation equations, and from this pair of equations, we calculate two expansions for the separation constant in terms of η. Equating the two expansions gives an estimate of α and, hence, all the parameters in the wave function ϕ_a. A brief account of the perturbation procedure is given in the Appendix, and further details may be found in Ref. [1]. The analysis of ϕ_b is carried out in the same way defining

$$p_2 = \frac{r_{2a} + r_{2b}}{R}, \quad q_2 = \frac{r_{2a} - r_{2b}}{R}, \quad \phi_b = \hat{X}(p_2)\hat{Y}(q_2), \tag{13}$$

and the analogous transformations are carried out, except that now, $y = 2\lambda(1 - q_2)$, corresponding to a zero-order situation where electron 2 is associated with the isolated atom B. The resulting approximation for ϕ_a takes the form

$$\begin{aligned} \phi_a &= N_a \exp[-\alpha R(p_1 - 1)] \exp[-\alpha R(1 + q_1)]\hat{\psi}_a \\ &= N_a \exp(-2\alpha r_{1a})\hat{\psi}_a \end{aligned} \tag{14}$$

expressed in either spheroidal or radial coordinates where $\hat{\psi}_a$ is a polynomial in $1/R$ and the variables (p_1,q_1) or (r_{1a},r_{1b}) such that $\hat{\psi}_a \to 1$ as $R \to \infty$; similarly for ϕ_b using (p_2,q_2) or (r_{2a},r_{2b}). In the regions where either electron 1 or electron 2 is far from both nuclei, these wave functions are equivalent to those used in the treatment of $H_2{}^+$ in Ref. [1] so that, asymptotically, when $E \approx 2\epsilon$, f is independent of these coordinates and approaches unity. In the nonasymptotic variational treatments of this system, the nonorthogonal coordinates generally used are the spheroidal coordinates defined above together with r_{12} and angular coordinate $\omega = \omega_1 + \omega_2$ where (ω_1,ω_2) are the angular coordinates of the separate spheroidal systems. For ground-state calculations, we take the azimuthal quantum numbers to be zero and do not need to include this dependence. (See, for example, James and Coolidge [3].) Consequently, we use symmetric and antisymmetric combinations of the asymptotic forms $\psi_A = \phi_a(p_1,q_1)\phi_b(p_2,q_2)f(r_{12})$ and $\psi_B = \phi_a(p_2,q_2)\phi_b(p_1,q_1)f(r_{12})$ to form singlet and triplet approximations, satisfying the Pauli principle. Use of these constructions implies that products of functions centered on the same atom may be ignored. This is equivalent to neglecting any contributions from the ionic structures H^+H^-,H^-H^+. The energies of these ionic functions are much higher than those of the atomic functions used, but this is counteracted by the Coulomb repulsion as R decreases (Pauling and Wilson [4]). However, here, we are considering large R, and these structures can be ignored.

The required approximation for f is found by a procedure similar to that used by Patil *et al.* [5]. For large R, we have, from Eq. (14),

$$\nabla_1\phi_a \sim -2\alpha\phi_a\hat{\mathbf{r}}_{1a}, \tag{15}$$

where $\hat{\mathbf{r}}_{1a}$ is the unit vector and the remaining terms in $\nabla_1\phi_a$ are of higher order in $\frac{1}{R}$. A similar calculation may be performed for $\nabla_2\phi_b$, and we have

$$\boldsymbol{\nabla} f(\phi_b\nabla_1\phi_a + \phi_a\nabla_2\phi_b) \sim -2\alpha R\boldsymbol{\nabla}\mathbf{f}\cdot(\hat{\mathbf{r}}_{1a} + \hat{\mathbf{r}}_{2b})\phi_a\phi_b. \tag{16}$$

The forms of both ϕ_a and ϕ_b [see Eq. (14)] show that they are strongly polarized near the internuclear axis where $p_1 = p_2 = 1$, and we have

$$\begin{aligned} \mathbf{r}_{1a} &= a_1\mathbf{i} + a_2\mathbf{j} + \frac{R}{2}(1 + q_1p_1)\mathbf{k}, \\ \mathbf{r}_{2b} &= b_1\mathbf{i} + b_2\mathbf{j} - \frac{R}{2}(1 - q_2p_2)\mathbf{k}, \end{aligned} \tag{17}$$

where, in the region $p_1 \approx 1 \approx p_2$, the a_j and b_j are small. These vectors are predominantly in the directions $\pm\mathbf{k}$, that is, along the internuclear axis. Patil *et al.* [5] use this result to approximate the scalar products so that

$$\hat{\mathbf{r}}_{12}\cdot\hat{\mathbf{r}}_{1a} = -1, \quad \hat{\mathbf{r}}_{21}\cdot\hat{\mathbf{r}}_{2b} = -1, \quad \boldsymbol{\nabla} f = \frac{\partial f}{\partial r_{12}}\hat{\mathbf{r}}_{12} = \frac{\partial f}{\partial r_{21}}\hat{\mathbf{r}}_{21}, \tag{18}$$

and, for large R, we have $E \approx 2\epsilon$ since the energy approaches the sum of energies of the isolated systems. Thus, the equation for f may be approximated in the form

$$-\frac{1}{2}\nabla^2 f + \frac{1}{r_{12}}f - 4\alpha\frac{\partial f}{\partial r_{12}} = 0. \tag{19}$$

Writing $r_{12} = r$, we have

$$-\tfrac{1}{2}\nabla_1^2 f = -\tfrac{1}{2}\nabla_2^2 f, \tag{20}$$

and, consequently,

$$[rD^2 + (2 + 4\alpha r)D - 1]f = 0, \quad D = \frac{d}{dr}. \tag{21}$$

Changing variables to $w = -4\alpha r$ leads to the standard Kummer equation [6],

$$L\left(w,2,-\frac{1}{4\alpha}\right) f = \left[w D_w^2 + (2-w)D_w + \frac{1}{4\alpha}\right] f = 0. \tag{22}$$

Since we require the solution to be finite at $r = 0$, we have the solution in terms of the Kummer M function,

$$f = M\left(\frac{-1}{4\alpha},2,-4\alpha r\right) = 1 + \frac{1}{2}r + \cdots . \tag{23}$$

In the analysis considered here, we require that the variables lie on a surface and are related by $q_1 = q_2$, and in this case,

$$\begin{aligned}\mathbf{r}_{12} &= -\mathbf{r}_{1a} + R\mathbf{k} + \mathbf{r}_{2b}\\ &= (b_1 - a_1)\mathbf{i} + (b_2 - a_2)\mathbf{j} + q(p_2 - p_1)\mathbf{k},\end{aligned} \tag{24}$$

where q is the common value of q_1 and q_2 so that all the elements will be small and *the component along the internuclear axis will not necessarily be dominant*. However, this does indicate that, in the dominant region, r_{12} is small so that an expansion in powers of r_{12} are a suitable approximation. From such an expansion of the full equation for f [Eq. (4)], we obtain the same first two terms as from the Kummer equation, namely,

$$f = 1 + \tfrac{1}{2}r_{12} + \cdots , \quad f > 1. \tag{25}$$

This result is *independent* of the values of E, $\hat{\mathbf{r}}_{12}\cdot\hat{\mathbf{r}}_{1a}$, and $\hat{\mathbf{r}}_{12}\cdot\hat{\mathbf{r}}_{2b}$ so that, as a first approximation in the most significant region on the surface where p_1 and p_2 are close to unity, we may take $f \approx 1$.

III. ESTIMATING THE EXCHANGE ENERGY USING THE HERRING-HOLSTEIN PROCEDURE

In order to use the Herring-Holstein [7,8] result, we write

$$\psi_\pm = \frac{1}{\sqrt{2}}(\psi_A \pm \psi_B), \tag{26}$$

and we need to choose a surface in the six-dimensional space and the conventional one is $z_1 = z_2$. Here, because the calculations are in spheroidals, we choose $q_1 = q_2$. Changing the coordinates to $2u = q_1 - q_2$, $2v = q_1 + q_2$, the surface S may be described as $u = 0$. Furthermore, since $q_1 = u + v$, $q_2 = v - u$, then, on S, we have

$$\begin{aligned}\psi_A &= N_{ab}\exp[-\alpha R(p_1 - 1)]\exp[-\alpha R(p_2 - 1)]\\ &\quad\times \exp(-2\alpha R)\exp(-2\alpha R u)\hat{\psi}_A f(r_{12}),\end{aligned} \tag{27}$$

and $\hat{\psi}_A$ is a polynomial in $v,u,p_1 - 1,p_2 - 1$, symmetric in p_1 and p_2. We note that $\alpha = \frac{1}{2} + O(R^{-1})$, and r_{12} is symmetric in the interchange of q_1,q_2 and, hence, *even* in u. Consequently, we may deduce

$$\left\{\frac{\partial r_{12}}{\partial u}\right\}_{u=0} = 0 \Rightarrow \left\{\frac{\partial f}{\partial u}\right\}_{u=0} = 0. \tag{28}$$

(See details in the Appendix.)

The analogous result for ψ_B is

$$\begin{aligned}\psi_B &= N_{ab}\exp[-\alpha R(p_1 - 1)]\exp[-\alpha R(p_2 - 1)]\\ &\quad\times \exp(-2\alpha R)\exp(2\alpha R u)\hat{\psi}_B f(r_{12}),\end{aligned} \tag{29}$$

and $\hat{\psi}_B$ is identical with $\hat{\psi}_A$, except that u is replaced by $-u$. Thus, we may deduce that, on S,

$$\psi_A = \psi_B, \quad \frac{\partial\psi_A}{\partial u} = -\frac{\partial\psi_B}{\partial u} \Rightarrow \nabla\psi_A\cdot\mathbf{e}_u = -\nabla\psi_B\cdot\mathbf{e}_u, \tag{30}$$

where $\mathbf{e}_u$ is the unit vector normal to S in the direction of increasing u. The symmetric and antisymmetric states satisfy

$$\left(-\tfrac{1}{2}\nabla^2 + \hat{V}\right)\psi_\pm = E_\pm\psi_\pm. \tag{31}$$

We may now consider the hypervolume $V = \{u < 0\}$ and may derive

$$\frac{1}{2}\int_V(\psi_+\nabla^2\psi_- - \psi_-\nabla^2\psi_+)dV = (E_+ - E_-)\int_V \psi_+\psi_- dV. \tag{32}$$

Substituting for ψ_A,ψ_B, we may deduce that

$$\int_V(\psi_B\nabla^2\psi_A - \psi_A\nabla^2\psi_B)dV = (E_+ - E_-)\int_V\left(\psi_A^2 - \psi_B^2\right)dV. \tag{33}$$

We may then deduce

$$\begin{aligned}&\int_V \nabla(\psi_B\nabla\psi_A - \psi_A\nabla\psi_B)dV\\ &\quad= (E_+ - E_-)\int_V\left(\psi_A^2 - \psi_B^2\right)dV,\end{aligned} \tag{34}$$

and using Green's theorem,

$$\int_S(\psi_B\nabla\psi_A - \psi_A\nabla\psi_B)\cdot d\mathbf{S} = (E_+ - E_-)\int_V\left(\psi_A^2 - \psi_B^2\right)dV, \tag{35}$$

which, by using Eq. (30), reduces to

$$\begin{aligned}2\int_S \psi_A\nabla\psi_A\cdot d\mathbf{S} &= (E_+ - E_-)\int_V\left(\psi_A^2 - \psi_B^2\right)dV\\ &\approx (E_+ - E_-)\int_V \psi_A^2 dV,\end{aligned} \tag{36}$$

since only ψ_A^2 is significant within V. The scale factors for the six-dimensional coordinates $p_1,p_2,u,v,\omega_1,\omega_2$ are given in the Appendix, but on S, we have $h_u = h_v$, and since

$$\nabla\psi_A\cdot\mathbf{e}_u = \frac{1}{h_u}\frac{\partial\psi_A}{\partial u}, \tag{37}$$

the surface integral on the left-hand side of Eq. (34) becomes

$$\begin{aligned}&(\pi)^2\frac{R^4}{2}\int_{u=0}\Psi_A\frac{\partial\psi_A}{\partial u}\sqrt{\left(p_1^2 - v^2\right)\left(p_2^2 - v^2\right)}\\ &\quad\times(1 - v^2)dp_1dp_2dv,\end{aligned} \tag{38}$$

where we have integrated over the angles ω_j. This integral can be expanded in inverse powers of R, using MAPLE; the details of this calculation are given in the Appendix. Here, we examine the form of the leading term in the exchange interaction. Since we require ψ_A to approach the product of the wave functions of two isolated hydrogen atoms for large R, we have $N_{ab} = \frac{1}{\pi}$ and since f does not contribute to the derivative [see Eq. (28)], we can take a mean value of $\bar{f} \approx 1$. The form of $\hat{\psi}_A$ is $F(u,v)F(-u,v)H(p_1)H(p_2)$ so that it is even in u and, consequently,

$$\left\{ \frac{\partial \hat{\psi}_A}{\partial u} \right\}_{u=0} = 0. \tag{39}$$

Thus, we have

$$\frac{\partial \psi_A}{\partial u} = -2R\alpha\psi_A, \tag{40}$$

and using $\alpha \approx \frac{1}{2}$ ($\alpha = \frac{1}{2}$ corresponds to unpolarized functions), we may approximate Eq. (38) by

$$-\frac{R^5}{2}\bar{f}^2 \exp(-2R) \int_{u=0} \exp[-R(p_1-1)] \exp[-R(p_2-1)] \times G(p_1,p_2,v)dp_1dp_2dv, \tag{41}$$

where G is a polynomial in the variables p_1,p_2,v. Now, since

$$\int_{p=1}^{\infty} \exp[-R(p-1)](p-1)^m dp = \frac{m!}{R^{m+1}} \tag{42}$$

for any non-negative integer m, the leading term of Eq. (41) is given by setting $p_1 = p_2 = 1$ in G. From this, we obtain

$$\begin{aligned} &-\frac{R^5}{2}\bar{f}^2 \exp(-2R) \int_{u=0} \exp[-R(p_1-1)] \exp[-R(p_2-1)] G(1,1,v) dp_1 dp_2 dv \\ &= -KR^5 \exp(-2R) \int_{p_1=1}^{\infty} \int_{p_2=1}^{\infty} \exp[-R(p_1-1)] \exp[-R(p_2-1)] dp_1 dp_2 = -KR^3 \exp(-2R) \end{aligned} \tag{43}$$

for some constant K. This is the same leading asymptotic form as in the Heitler-London result [Eq. (5)]. It is also the same order as obtained by Tang *et al.* [9] in calculations for lower values of R using the Herring-Holstein technique with the lowest $1s$-state atomic wave functions. The analysis of Eq. (38) in the Appendix gives the explicit asymptotic approximation,

$$\begin{aligned} &\frac{1}{2}(E_+ - E_-) \\ &\quad = -R^3 \exp(-2R) \left(0.150\,836 + \frac{1.227\,85}{R} + \cdots \right) \\ &\quad = O(R^3 \exp(-2R)), \end{aligned} \tag{44}$$

where, from Eq. (24), taking that r_{12} is small in the dominant region into account, we use $\bar{f} = 1$. Equation (44) is obtained by expressing the parameter α as an expansion in inverse powers of R, and the terms from the perturbation of ϕ_a and ϕ_b can be obtained from a higher order. In addition, the volume integral has been estimated using $\psi_A \approx \phi_a\phi_b$ with this value of α rather than the localized $1s$ ground-state wave functions for the isolated atoms. The functions ϕ_a,ϕ_b are also localized about atoms A and B, respectively, so that the effect of r_{12} is negligible, but they are polarized functions that take the presence of the other atom into account. We note that, on the surface $u = 0$, at points such that $p_1 = p_2 = 1$ where the contribution of $\phi_a\phi_b$ is greatest, we have $r_{12} = 0$. The exponential form of the integrand in the surface integral implies that it is dominated by the integral over the restricted region described by $1 \leqslant p_1 \leqslant \rho$, $1 \leqslant p_2 \leqslant \rho$, and we may choose ρ so that $\rho \to 0$ as $R \to \infty$ in any manner. Since

$$\lim_{\rho \to 0} r_{12}(u=0) = 0 \Rightarrow \lim_{\rho \to 0} f = 1, \tag{45}$$

we may deduce that *the lowest term* in Eq. (44) is valid.

The main advantage of Eq. (44) is that it does not contain the unphysical term in $\ln(R)$, which has a major effect for *very large* R. Herring and Flicker [2] give an alternative asymptotic approximation with a leading term of different order, but their estimate agrees with the Heitler-London estimates in the range of R for which the splitting is on the order of hundredths to millionths of an electron volt. The result in Ref. [2] is obtained by using an analogous form of an asymptotic approximation to Eq. (2), but instead of ϕ_a,ϕ_b used here, they use ϕ_a^0,ϕ_b^0, which are the ground-state $1s$ wave functions for the isolated hydrogen systems. The corresponding function f is found by writing it in the form $f = \exp(-B)$, substituting into Eq. (4) (with the $1s$ functions rather than the polarized functions considered here), and neglecting the terms,

$$\kappa = \tfrac{1}{2}(\nabla^2 B - |\nabla B|^2). \tag{46}$$

This is corrected perturbatively, and the authors consider a restricted region $\rho_1,\rho_2 \leqslant R^{1/2}$, where ρ_1 and ρ_2 are the distances of electrons 1 and 2 from the internuclear axis. They show that the correction to κ is $O(r_{12}^{-2})$ and argue that the effect on the perturbation equation for B is less than $O(r_{12}^{-1})$ for most of the restricted region, although they point out that the corrected terms are wrong in the region of small r_{12}. We have found that the most significant contribution to the surface integral for the exchange energy arises from the subregion where $\rho_1 \approx \rho_2 \approx 0$. In this subregion, on both the surface used by Herring and Flicker ($z_1 = z_2$) and the surface used here ($q_1 = q_2$), we have $r_{12} \approx 0$. Thus, the order of the correction to B derived by Herring and Flicker will be large and cannot be justifiably neglected. The result obtained by Herring and Flicker takes the form

$$\tfrac{1}{2}(E_+ - E_-) = -0.821 R^{2.5} \exp(-2R) + O(R^2 \exp(-2R)), \tag{47}$$

so that, even though it gives the same order of magnitude as for the Heitler-London result for some intervals of large R, it is at odds with the asymptotic leading term of both the Heitler-London result and the approximation obtained here. In Figs. 1 and 2, we illustrate the differences between the three formulas. In Fig. 1, we plot the three formulas in the range of $90 < R < 100$; the upper curve is the Heitler-London formula,

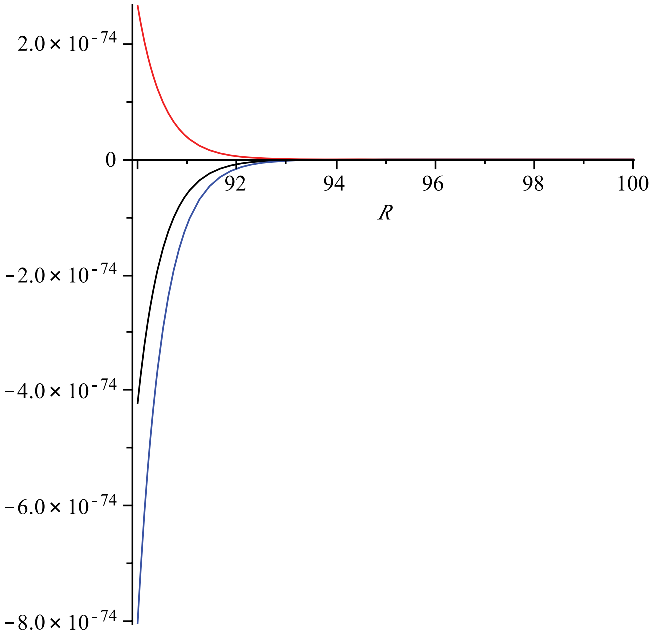

FIG. 1. (Color online) The exchange energy $\Delta E = \frac{1}{2}(E_+ - E_-)$ is plotted for the three formulas in the range of $90 < R < 100$. The upper curve is the Heitler-London formula, the middle curve is the Herring-Flicker formula, and the lower curve is obtained from the formula derived here [Eq. (44)] (energies and separations in a.u.).

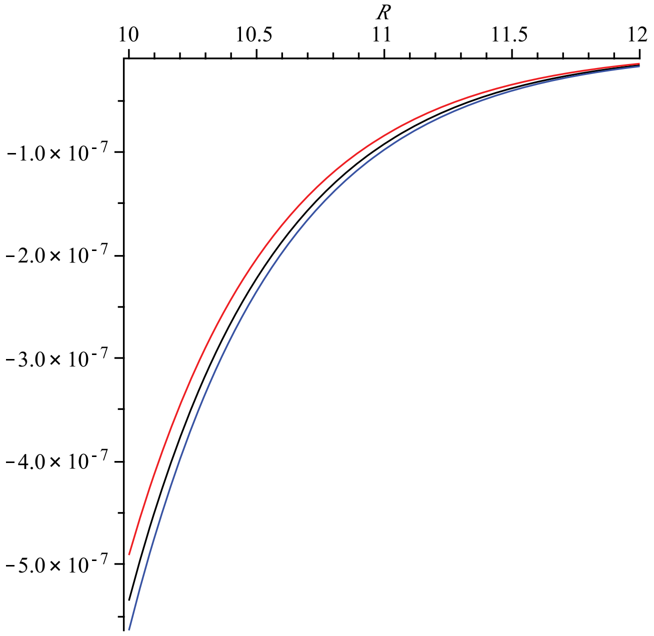

FIG. 2. (Color online) The exchange energy $\Delta E = \frac{1}{2}(E_+ - E_-)$ is plotted for the three formulas in the range of $10 < R < 12$. The upper curve is the Heitler-London formula, the middle curve is the Herring-Flicker formula, and the lower curve is obtained from the formula derived here [Eq. (44)] (energies and separations in a.u.).

the lower curve is our formula, and the middle curve is the Herring-Flicker result. For this range of very large values of R, we see that, although our formula gives larger magnitudes, it is fairly consistent with the Herring-Flicker formula; the Heitler-London formula has the wrong sign. In Fig. 2, the formulas are plotted in the range of $10 < R < 12$, and the two lower graphs, which correspond to our formula and to the Herring-Flicker formula, are almost coincident. The upper graph is also close in this range so that all three approximately give the same exchange energies. This indicates that our approximation $f \approx 1$ is not only valid asymptotically, but also gives results consistent with the Heitler-London treatment for smaller values of R where the variational approach is expected to be more accurate.

This is supported by the paper of Tang *et al.* [9] who do not consider the effect of r_{12} but use unpolarized atomic orbitals for hydrogen to compare with exact *ab initio* calculations [10,11] and show that their results are in line with the Heitler-London calculations. In Table I, we compare the results in Refs. [10,11] with the results in Ref. [9] and with calculations from our Eq. (44). Generally, our values are closer to the *ab initio* values [10,11], even though Eq. (44) is just the first two terms of an expansion in powers of R^{-1}, which may be expected to be more accurate asymptotically; for small R, the ionic terms may be more important, and the error in the perturbation expansion may be larger. The main advantage of our result is that we use polarized orbitals, and it is well known from calculations on H_2^+ that it is essential that polarized orbitals are used in order to obtain accurate results. The range of R in Table I is $1 \leqslant R \leqslant 12$, whereas, our analysis indicates that the effect of the nonphysical term in the Heitler-London formula is only substantial for much larger R's.

From Eq. (25), by using the approximation $f \approx 1 + \frac{1}{2}r_{12}$, we may neglect the last term in Eq. (4), and consequently, the equation for $\phi_a\phi_b$ is

$$\left(-\frac{1}{2}\nabla^2 - \frac{1}{r_{1a}} - \frac{1}{r_{1b}} - \frac{1}{r_{2a}} - \frac{1}{r_{2b}}\right)\phi_a\phi_b = 2\epsilon\phi_a\phi_b, \qquad (48)$$

and any approximation of the solution of this equation does not involve integrals over $\frac{1}{r_{12}}$. The nonphysical term in the Heitler-London result is obtained from the integral,

$$\int \frac{\phi_a(1)\phi_a(2)\phi_b(1)\phi_b(2)}{r_{12}}dV, \qquad (49)$$

TABLE I. Comparison of the results from Ref. [9] and the calculations from our Eq. (44) with the exact results from Refs. [10,11].

R	Ref. [9]	Eq. (44)	Exact
1	$-2.709 \times 10^{-1}(0.93)$	$-1.866 \times 10^{-1}(1.35)$	-2.515×10^{-1}
1.4	$-1.938 \times 10^{-1}(1.01)$	$-1.715 \times 10^{-1}(1.14)$	-1.952×10^{-1}
2	$-1.081 \times 10^{-1}(1.12)$	$-1.121 \times 10^{-1}(1.08)$	-1.206×10^{-1}
3	$-3.462 \times 10^{-2}(1.23)$	$-3.749 \times 10^{-2}(1.14)$	-4.265×10^{-2}
4	$-9.355 \times 10^{-3}(1.23)$	$-9.829 \times 10^{-3}(1.17)$	-1.150×10^{-2}
5	$-2.275 \times 10^{-3}(1.12)$	$-2.250 \times 10^{-3}(1.13)$	-2.550×10^{-3}
6	$-5.010 \times 10^{-4}(1.02)$	$-4.718 \times 10^{-4}(1.08)$	-5.105×10^{-4}
7	$-1.030 \times 10^{-4}(0.94)$	$-9.305 \times 10^{-5}(1.04)$	-9.680×10^{-5}
8	$-2.012 \times 10^{-5}(0.88)$	$-1.753 \times 10^{-5}(1.01)$	-1.765×10^{-5}
9	$-3.773 \times 10^{-6}(0.83)$	$-3.189 \times 10^{-6}(0.98)$	-3.120×10^{-6}
10	$-6.855 \times 10^{-7}(0.78)$	$-5.640 \times 10^{-7}(0.95)$	-5.375×10^{-7}
11	$-1.212 \times 10^{-7}(0.75)$	$-9.745 \times 10^{-8}(0.93)$	-9.100×10^{-8}
12	$-2.097 \times 10^{-8}(0.76)$	$-1.651 \times 10^{-8}(0.97)$	-1.600×10^{-8}

and, consequently, does not arise if Eq. (48) is used. The approximation for f is suitable for a calculation using the Herring-Holstein technique since the most significant region is near the midpoint of the internuclear line where $r_{12} \approx 0$, but for a variational calculation over all spaces, the effect of the dependence on r_{12} may be expected to be more important. The values in the brackets are the ratios of the results from Ref. [9] or Eq. (44) to the exact values in Refs. [10,11].

IV. CONCLUDING REMARKS

The main purpose of this paper was to develop techniques that can be used to treat asymptotic valence interactions involving two electrons, extending our earlier paper on exchange calculations. The example of H_2 for large R is a prototype for such work, and we have developed formulas similar to those in our previous paper, taking the dependence on r_{12} and the Pauli principle into account. We found that our approximate formulas gave similar results to those found by the standard Heitler-London variational calculations but without the unphysical term for larger R's that it contained. The formula that we obtained gave comparable results to the formula derived by Herring and Flicker, but the behaviour for large R differed.

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APPENDIX: SOME DETAILS

1. Algebraic perturbation theory

We begin with a realization of the SO(2,1) Lie algebra generators given by

$$J_- = xD^2 + D, \quad J_0 = xD + \tfrac{1}{2}, \quad J_+ = x, \tag{A1}$$

where $D = \frac{d}{dx}$ and Eq. (10) of the text may be expressed in terms of these operators,

$$\begin{aligned}&\left(J_- - J_0 - \left(\gamma - \tfrac{1}{2}\right)\right)\Phi \\ &\quad = -\eta\left(J_0 - \tfrac{1}{2} + J_+\left(J_- - J_0 + \tfrac{1}{2} - s\right)\right)\Phi.\end{aligned} \tag{A2}$$

Using a similarity transformation, $\exp(J_-)$ transforms the operators to

$$J_0 \to J_0 + J_-, \quad J_+ \to J_+ + 2J_0 + J_-, \tag{A3}$$

and the equation to

$$\begin{aligned}&(h_0 + \eta h_1)\hat{\Phi} = \gamma\hat{\Phi}, \quad h_0 = \tfrac{1}{2} - J_0, \\ &\qquad h_1 = (J_+ + 2J_0 + J_-)(b + h_0) + J_- - h_0,\end{aligned} \tag{A4}$$

where $b = \frac{1}{\alpha} - 1$. Perturbation theory is then used in powers of η. From the algebraic structure of this perturbation equation, it is convenient to express the operators in terms of their matrix representations in the basis $\{x^n, n = 0,1,2,\ldots\}$ so that we obtain a matrix perturbation equation of the form

$$H_0\mathbf{x} = (\Gamma - \eta H_1)\mathbf{x}, \tag{A5}$$

with the zero order $\Gamma_0 = 0$, $\mathbf{x}_0^T = (1,0,0,\ldots)$, corresponding to the appropriate equation for the isolated hydrogen. The higher-order values of Γ and the wave function are obtained by ensuring consistency of the equations and choosing the higher-order wave functions to have no component in the zero-order function. An essentially equivalent procedure is carried out for Eq. (12), and the separation constant can be expressed in terms of Γ from Eq. (11) (for all orders) and δ from Eq. (12). Equating the expressions for C gives a nonlinear equation in R and α. To obtain an approximate asymptotic wave function in terms of R, it is necessary to express α in terms of R. This was performed by solving the nonlinear equation for α for a set of values of R and expressing α as a polynomial in $\frac{1}{R}$; we used a fitting at $R = 80,90,100$ to obtain

$$\alpha = 0.5 + \frac{0.5}{R} - \frac{0.241}{R^2}. \tag{A6}$$

The estimates from this formula were found to be accurate for a wide range of values of R from 8 to 100, but for more precise calculations in the ranges of R in this interval, the fitting points can be varied. Given expression (A6) for α, the perturbed wave functions are obtained in terms of R using MAPLE.

2. The derivative of r_{12}

The surface $u = 0$ divides the six-dimensional space into two parts with atom A on one side and atom B on the other symmetrically. The Cartesian coordinates in the six-dimensional space can be written in terms of two sets of spheroidal coordinates (one set for each of the two electrons), and we perform the further transformations used in the main text: $q_1 = u + v$, $q_2 = v - u$. In this section, we take origin O to be the same for both sets of spheroidal coordinates and choose $p_1 = p_2 = 1$, $v = u = 0$. Thus, we have

$$\begin{aligned}x_1 &= \frac{R}{2}\sqrt{p_1^2 - 1}\sqrt{1 - (u+v)^2}\cos(\omega_1), \\ x_2 &= \frac{R}{2}\sqrt{p_2^2 - 1}\sqrt{1 - (v-u)^2}\cos(\omega_2), \\ y_1 &= \frac{R}{2}\sqrt{p_1^2 - 1}\sqrt{1 - (u+v)^2}\sin(\omega_1), \\ y_2 &= \frac{R}{2}\sqrt{p_2^2 - 1}\sqrt{1 - (v-u)^2}\sin(\omega_2), \\ z_1 &= \frac{R}{2}p_1(v+u), \quad z_2 = \frac{R}{2}p_2(v-u).\end{aligned} \tag{A7}$$

Forming

$$\begin{aligned}&r_{12}(p_1,p_2,u,v,\omega_1,\omega_2) \\ &\quad = \sqrt{(x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2},\end{aligned} \tag{A8}$$

we can use MAPLE to simplify the expression and to observe that r_{12} is even in u so that

$$\left\{\frac{\partial r_{12}}{\partial u}\right\}_{u=0} = 0. \tag{A9}$$

For origin O, because of the singular nature of the derivative of the square root at 0, it is necessary to interpret Eq. (A9) as

$$\lim_{P \to O}\left\{\frac{\partial r_{12}}{\partial u}\right\}_{u=0} = 0 \tag{A10}$$

for points $P(\neq O)$. This is completely analogous to the interpretation of the following one-dimensional derivative calculation when $a = 0$:

$$\lim_{a\to 0}\left\{\frac{d}{dx}\sqrt{a^2+x^2}\right\}_{x=0} = 0 \neq \left\{\frac{d}{dx}\left\{\lim_{a\to 0}\sqrt{a^2+x^2}\right\}\right\}_{x=0}. \tag{A11}$$

3. Scale factors for the surface integration

The analysis here is based on considering a general vector $\mathbf{r}$ expressed in terms of a set of *orthogonal* coordinates in any number of dimensions. Moving along one of these coordinates η, say we have

$$\frac{\partial \mathbf{r}}{\partial \eta} = h_\eta \mathbf{e}_\eta, \tag{A12}$$

where $\mathbf{e}_\eta$ is the coordinate-dependent unit vector along the η curve with all other variables held fixed. Thus,

$$\left|\frac{\partial \mathbf{r}}{\partial \eta}\right| = h_\eta, \tag{A13}$$

and this makes a contribution $h_\eta d\eta$ to the volume element. Additionally, we require

$$\nabla \cdot \mathbf{e}_\eta = \frac{1}{h_\eta}\frac{\partial}{\partial \eta}, \tag{A14}$$

since

$$\nabla = \sum_\eta \mathbf{e}_\eta \frac{1}{h_\eta}\frac{\partial}{\partial \eta}. \tag{A15}$$

We need two sets of spheroidal coordinates $\{(p_1,q_1,\omega_1),(p_2,q_2,\omega_2)\}$. But we want these on the surface $q_1 = q_2$ so that, using the transformed coordinates, the general six-dimensional vector $\mathbf{r}^T = (\mathbf{r}_{1a},\mathbf{r}_{2b})^T$ can be written

$$\begin{aligned}\mathbf{r}^T = \frac{R}{2}\Big(&\sqrt{(p_1^2-1)[1-(u+v)^2]}\cos(\omega_1),\\ &\sqrt{(p_1^2-1)[1-(u+v)^2]}\sin(\omega_1), p_1(u+v)+1,\\ &\sqrt{(p_2^2-1)[1-(v-u)^2]}\cos(\omega_2),\\ &\sqrt{(p_2^2-1)[1-(v-u)^2]}\sin(\omega_2), p_2(v-u)-1\Big).\end{aligned} \tag{A16}$$

All the necessary partial derivatives can be calculated from (A16). For example,

$$\begin{aligned}\frac{\partial \mathbf{r}^T}{\partial p_1} = \frac{R}{2}\Bigg(&\frac{p_1}{\sqrt{p_1^2-1}}\sqrt{1-(u+v)^2}\cos(\omega_1),\\ &\frac{p_1}{\sqrt{p_1^2-1}}\sqrt{1-(u+v)^2}\sin(\omega_1),(u+v),0,0,0\Bigg),\end{aligned} \tag{A17}$$

so that, *on* $u = 0$, we have

$$\left|\frac{\partial \mathbf{r}^T}{\partial p_1}\right|^2 = \frac{R^2}{4}\left[\frac{p_1^2}{p_1^2-1}(1-v^2)+v^2\right], \tag{A18}$$

which leads to

$$h_{p_1} = \frac{R}{2}\frac{1}{\sqrt{p_1^2-1}}\sqrt{p_1^2-v^2}. \tag{A19}$$

The calculation of h_{p_2} is similar. There are a few sign differences, but finally,

$$h_{p_2} = \frac{R}{2}\frac{1}{\sqrt{p_2^2-1}}\sqrt{p_2^2-v^2}. \tag{A20}$$

Using the same technique,

$$\begin{aligned}\frac{\partial \mathbf{r}^T}{\partial \omega_1} = \frac{R}{2}\big\{&\sqrt{p_1^2-1}\sqrt{1-(u+v)^2}[-\sin(\omega_1)],\\ &\sqrt{p_1^2-1}\sqrt{1-(u+v)^2}\cos(\omega_1),0,0,0,0\big\},\end{aligned} \tag{A21}$$

leading to

$$h_{\omega_1} = \frac{R}{2}\sqrt{p_1^2-1}\sqrt{1-v^2}, \tag{A22}$$

and similarly for h_{ω_2} with p_2 replacing p_1. The more complicated calculation is

$$\begin{aligned}\frac{\partial \mathbf{r}^T}{\partial u} = \frac{R}{2}\Bigg(&-\frac{\sqrt{p_1^2-1}\cos(\omega_1)(u+v)}{\sqrt{1-(u+v)^2}},\\ &-\frac{\sqrt{p_1^2-1}\sin(\omega_1)(u+v)}{\sqrt{1-(u+v)^2}},p_1,\\ &-\frac{\sqrt{p_2^2-1}\cos(\omega_2)(v-u)}{\sqrt{1-(v-u)^2}},\\ &-\frac{\sqrt{p_2^2-1}\sin(\omega_2)(v-u)}{\sqrt{1-(v-u)^2}},-p_2\Bigg).\end{aligned} \tag{A23}$$

The analogous calculation above of h_u gives

$$h_u = \frac{R}{2}\frac{\sqrt{p_1^2+p_2^2-2v^2}}{\sqrt{1-v^2}}. \tag{A24}$$

The calculation for h_v again involves some differences in signs but is finally the same. *That is, at* $u = 0$, $h_u = h_v$. For the Herring-Holstein result, we need

$$\int_{u=0} h_{p_1}h_{p_2}h_{\omega_1}h_{\omega_2}h_v \Psi_A \nabla\Psi_A \cdot \mathbf{e}_u dS. \tag{A25}$$

Now,

$$\nabla\Psi_A \cdot \mathbf{e}_u = \frac{1}{h_u}\frac{\partial \Psi_A}{\partial u}, \tag{A26}$$

where it is understood that, throughout, we have $u = 0$. But we know that, at $u = 0$, we may use the identity $h_u = h_v$ with the appropriate limits and so, integrating over the angles gives

$$4(\pi)^2\int_1^\infty\int_1^\infty\int_{-1}^1 \Psi_A \frac{\partial \Psi_A}{\partial u} h_{p_1}h_{p_2}h_{\omega_1}h_{\omega_2}dp_1dp_2dv. \tag{A27}$$

The product of the scale factors is

$$h_{p_1}h_{p_2}h_{\omega_1}h_{\omega_2} = \frac{R^4}{16}\sqrt{p_1^2 - v^2}\sqrt{p_2^2 - v^2}(1 - v^2). \tag{A28}$$

To evaluate the integral, we expand

$$\sqrt{p_1^2 - v^2} = p_1\sqrt{1 - \left(\frac{v}{p_1}\right)^2}, \tag{A29}$$

first, in terms of $\frac{v}{p_1}$ with $p_1 \geqslant 1$, $|v| \leqslant 1$ and then, in terms of powers of $(p_1 - 1)$. The form of the approximate wave function is a product of exponentials in p_1, p_2 times polynomials in $(p_1 - 1),(p_2 - 1), v$ with coefficients depending on $\frac{1}{R}$ so that the integration over p_1 may then be carried out analytically term by term. A similar analysis may be performed for p_2 so that the final integral is a simple polynomial over v. This was carried out using MAPLE, but in order to obtain the final result in terms of R, it was necessary to express the exponent α in terms of R, and we used the expansion in Eq. (A6). To obtain formulas for the exchange in different ranges of R, it is possible to change the fitting points used in deriving this expansion, but we need R to be large for the validity of the process. The exponent α also has a significant effect on the volume integral. If the 1s functions are used instead of ϕ_a, ϕ_b, then this can be evaluated as $1 + O(\exp(-2R))$, but in our case, 1 is replaced by the form

$$1 + \frac{c_1}{R} + \frac{c_2}{R^2} + \cdots . \tag{A30}$$

The calculation of the volume integral is carried out straightforwardly in MAPLE using two sets of spheroidal coordinates and, again, making use of the expansion of α in terms of R.

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