Asymptotic Exchange Coupling of Two Hydrogen Atoms

Conyers Herring and Michael Flicker*

Bell Telephone Laboratories, Murray Hill, New Jersey

(Received 1 November 1963; revised manuscript received 3 January 1964)

The energy difference $2J$ between the lowest singlet and triplet states of the hydrogen molecule measures the exchange coupling of the spins of the two atoms. It is known that the Heitler-London expression for $2J$ is inaccurate, even at large interatomic distances R, because it takes inadequate account of the mutual avoidance of the exchanging electrons. Gor'kov and Pitaevski have recently shown that the leading term in the expression for $2J$ at large R can be evaluated exactly. The procedure involves treating the interaction of the two atoms as a perturbation on a product of single-atom wave functions. However, their final result differs by a numerical factor, and in the remainder term, from that of an independent though basically identical calculation of ours. It is shown here that the correct result is: $2J = -1.641\ R^{5/2}e^{-2R} + O(R^2 e^{-2R})$, where J is in atomic units (2Ry) and R is in Bohr units.

I. INTRODUCTION

THE concept of the exchange coupling of the spins of a cluster of nonsinglet atoms arose about a third of a century ago in the Heitler-London theory[1] of molecular binding and the Heisenberg theory[2] of ferromagnetism. In a recent paper,[3] to be referred to as I, it has been shown that this concept can be given a rigorous justification for the case where the overlap of the wave functions of the different atoms is very slight. The rigorous formulation agrees with the conventional one in describing such a system by an effective Hamiltonian

$$H_{\text{eff}} = -2 \sum_{i>j} J_{ij}\mathbf{S}_i\cdot\mathbf{S}_j, \qquad (1)$$

where i, j run over the various atoms, each assumed to be in an orbitally nondegenerate state with spin operator $\mathbf{S}_i$. However, the correct coefficients J_{ij} are not the same as those computed by the Heitler-London approximation of considering as possible wave functions only the antisymmetrized products of isolated-atom functions. Physically, J_{ij} measures the rate at which an electron exchange would take place between atoms i and j if each atom started with a known set of individually distinguishable electrons. In the course of such an exchange process, the mutual avoidance of the exchanging electrons is bound to be important, and this correlation effect is ignored in the Heitler-London approximation.

The simplest possible real system to which (1) can be applied is a pair of hydrogen atoms. For this system Gor'kov and Pitaevski[4] have recently undertaken to calculate the asymptotic value of the exchange constant $J_{ij} \equiv J$ when the internuclear separation R is large compared with a Bohr radius. Their method of calcula-

tion, though worked out independently and rooted in a treatment of the H_2^+ problem by Landau,[5] is very similar to an approach outlined in I and to a treatment of the H_2^+ problem by Holstein.[6] Moreover, up to a certain point their method and their results coincide with those of a calculation, hitherto unpublished, which we carried out in 1962. Our result differs from theirs, however, in the numerical coefficient in the expression for J and in the algebraic form of the second (neglected) term in the asymptotic expansion. The purpose of the present paper is to describe these differences and to show that our result is the correct one.

In Sec. II we shall repeat, with addition of a few comments, the argument by whick Gor'kov and Pitaevski reduced the expression for J to a surface integral over a hyperplane in the 6-dimensional coordinate space. This surface integral is a special case of that introduced in I for the general problem of coupling of any number of many-electron atoms. Section III will be devoted to a perturbational solution of the wave equation for the asymmetrical wave function entering the surface-integral expression. This solution is also essentially identical with that obtained by Gor'kov and Pitaevski. The details of its derivation are necessary, however, for the critical discussion to be given in Sec. IV regarding the accuracy of the approximations used and the size to be expected for the next term in the asymptotic series for J. In Sec. V we shall perform the explicit evaluation of the leading term in the surface integral (actually a fivefold integration). This is the point at which Gor'kov and Pitaevski have erred. Section VI will give some concluding remarks and a quantitative and qualitative comparison with the Heitler-London expression for J.

II. THE SURFACE INTEGRAL FOR J

Let Φ_g, Φ_u be the exact solutions of the two-electron coordinate wave equation which are, respectively, sym-

---

* Present address: Belfer Graduate School of Science, Yeshiva University, New York, New York.

[1] W. Heitler and F. London, Z. Physik **44**, 455 (1927).

[2] W. Heisenberg, Z. Physik **49**, 619 (1928).

[3] C. Herring, Rev. Mod. Phys. **34**, 631 (1962).

[4] L. P. Gor'kov and L. P. Pitaevski, Dokl. Akad. Nauk SSSR **151**, 822 (1963) [English transl.: Soviet Phys.—Dokl. **8**, 788 (1964)].

[5] L. D. Landau and E. M. Lifshitz, *Kvantovaya Mekhanika* (Moscow, 1963). Apparently this is not yet commercially available in the United States.

[6] T. D. Holstein, Westinghouse Research Report 60-94698-3-R9, 1955 (unpublished).

metrical and antisymmetrical in the coordinates of the two electrons. The singlet and triplet wave functions are thus products of Φ_g, Φ_u, respectively, with appropriate spin functions. If the phases of Φ_g, Φ_u are properly chosen, the function

$$\Phi_1 = 2^{-1/2}(\Phi_g + \Phi_u) \qquad (2)$$

will be large only when electron 1 is near proton a and electron 2 near proton b. Let us define Σ to be the hyperplane, in the six-dimensional coordinate space, on which

$$r_{a1}{}^2 + r_{b2}{}^2 = r_{b1}{}^2 + r_{a2}{}^2 ,$$

where the r's denote the distances between the particles designated by the subscripts. If we take the z direction along the internuclear line ab, this equation is equivalent to

$$z_1 = z_2 \quad \text{on} \quad \Sigma . \qquad (3)$$

Then Φ_1 is localized almost entirely on one side—let us call it the "near" side— of Σ, while the function $P\Phi_1$, obtained by permuting $\mathbf{r}_1$ with $\mathbf{r}_2$ in Φ_1, is localized almost entirely on the "far" side. It is easily verified that, if we use atomic units and let ∇ designate the six-dimensional gradient, so that the kinetic energy operator is $-\frac{1}{2}\nabla^2$,

$$\int_{\text{near}} d^6 r (\Phi_u H \Phi_g - \Phi_g H \Phi_u)$$
$$= \frac{1}{2} \int_{\Sigma} d\mathbf{S} \cdot [(P\Phi_1)\nabla\Phi_1 - \Phi_1\nabla(P\Phi_1)] , \quad (4)$$

where $d\mathbf{S}$ is the surface element of Σ times the unit normal directed from "near" to "far." The left of (4) is the singlet-triplet splitting $\mathscr{E}_g - \mathscr{E}_u$ times the integral of $\Phi_g \Phi_u$ over the "near" region, which latter is $\frac{1}{2} + O(e^{-2R})$, R being the internuclear distance. The two terms on the right of (4) are equal, so we have finally for the exchange constant

$$J \equiv \frac{1}{2}(\mathscr{E}_g - \mathscr{E}_u) = \int_{\Sigma} d\mathbf{S} \cdot (P\Phi_1)\nabla\Phi_1 + O(e^{-4R}) . \quad (5)$$

The Hamiltonian is, in our atomic units,

$$H = -\frac{1}{2}\nabla^2 - (1/r_{a1}) - (1/r_{b2})$$
$$+ (1/R) + (1/r_{12}) - (1/r_{a2}) - (1/r_{b1}) , \quad (6)$$

where 1, 2 represent the electrons, a, b the protons, and again ∇^2 is the 6-dimensional Laplacian. Since Φ_1 is nearly the same as the product of single-atom functions which describes the ground state of the operator on the first line of (6), we would like to use this as the starting point of a perturbational approximation to it. One may be disturbed by the fact that the perturbation represented by the second line of (6), though small on the "near" side of Σ, gets very large on the "far" side. However, a rigorous proof was given in I that J can be evaluated, to the accuracy of the neglected term in (5),

by replacing Φ_1 in (5) by the ground-state eigenfunction φ_1 in a potential V' coinciding with the true potential on the "near" side of Σ and for some little distance on the "far" side, but truncated so as to have no deep trough on the "far" side. The difference between V' and the potential in the first line of (6) is everywhere small, and can legitimately be treated as a perturbation.

III. PERTURBATIONAL SOLUTION FOR φ_1

Following a procedure originally applied by Holstein[6] to the $H_2{}^+$ problem, let us set

$$\varphi_1 = \exp(-S_0 - \Delta S) , \qquad (7)$$

where

$$\exp(-S_0) = \pi^{-1} \exp(-r_{a1} - r_{b2}) \qquad (8)$$

is the product of two isolated-atom eigenfunctions, and where ΔS describes the corrections due to the departure of the potential V', which occurs in the wave equation for φ_1, from the potential in the first line of (6). The differential equation for the exponent ΔS in (6) is

$$\frac{1}{2}\nabla^2 \Delta S - \frac{1}{2}|\nabla\Delta S|^2 - \nabla S_0 \cdot \nabla\Delta S + (\Delta V - \Delta\mathscr{E}) = 0 , \quad (9)$$

where ΔV is $V' + (1/r_{a1}) + (1/r_{b2})$, and $\Delta\mathscr{E}$ is the difference between the eigenvalue of φ_1 and the eigenvalue, -1 atomic unit, of e^{-S_0}. Now we expect ΔS to vary sizably only over distances of order R in the six-dimensional coordinate space, whereas S_0 varies sizably in a distance of a Bohr unit. It is therefore reasonable to hope that we can approximate ΔS adequately by the solution S_1 of the differential equation obtained from (9) by dropping the first two terms. Our procedure will thus be to solve this modified differential equation, and then to verify that our neglect of the first two terms is consistent. Such a procedure would not suffice for a calculation of the van der Waals energy, which depends on $1/R^3$ terms in ΔS at small r_{a1}, r_{b2}, but it will turn out to give the terms of order unity and $\ln r_{12}$ in S_1 correctly.

Since the term $\Delta\mathscr{E}$ in (9) is of the order of the van der Waals energy, hence $\propto R^{-6}$, we may neglect it in the equation for S_1. Treating S_1 as a function of the variables $r_{a1} \pm r_{b2}$ and the directions of $\mathbf{r}_{a1}$, $\mathbf{r}_{b2}$, this equation now reads

$$2[\partial S_1/\partial(r_{a1}+r_{b2})] = (1/R) + (1/r_{12})$$
$$- (1/r_{a2}) - (1/r_{b1}) \quad (10)$$

everywhere except where the right side is large and negative; in the latter regions V' is truncated, so the right of (10) is to be replaced by a quantity (say zero) which does not become large. Integration of (10) determines S_1 to within an arbitrary function of $(r_{a1} - r_{b2})$ and the angles. This function is determined by the condition that when $r_{a1} \to 0$ (or $r_{b2} \to 0$) the dependence of the wave function on r_{b2} (or r_{a1}) must approach that for a free atom, if we neglect the high powers of $1/R$ which enter into $\Delta\mathscr{E}$. Thus we have the boundary condition

$$S_1 = 0 \quad \text{for} \quad r_{a1} = 0 \quad \text{or} \quad r_{b2} = 0 . \qquad (11)$$

The integration of (10) subject to (11) is straight-forward, though tedious. The region where V' is truncated does not need to be considered explicitly, as we shall not need S_1 in this region; the truncation merely ensures that we need not worry about S_1 getting large and negative. Elsewhere, the solution is

$$S_1 = \frac{r_<}{R} \mp \ln \frac{r_<' + |r_< - R \cos\theta_<|}{R(1 \mp \cos\theta_<)} \mp \ln \frac{r_>' + |r_> - R \cos\theta_>|}{r^* \pm (r_> - r_< - R \cos\theta_>)}$$

$$\pm (2G)^{-1/2} \ln \frac{(2G)^{1/2} r_{12} + |G(r_{a1} + r_{b2}) - R(\cos\theta_1 + \cos_2)|}{(2G)^{1/2} r^* \pm [G(r_> - r_<) - R(\cos\theta_1 + \cos\theta_2)]}, \quad (12)$$

where $r_>$, $r_<$ are, respectively, the greater and lesser of r_{a1}, r_{b2}; $\theta_>$, $\theta_<$ are the corresponding polar angles, defined as shown in Fig. 1, so that they vanish if both electrons are on the internuclear line between a and b; $r_>'(r_<')$ is the distance of the electron involved in $r_>(r_<)$ from the other nucleus, i.e.,

$$r_{>,<}' = (r_{>,<}^2 + R^2 - 2r_{>,<}R \cos\theta_{>,<})^{1/2}; \quad (13)$$

$$r^* = [(r_{a1} - r_{b2})^2 + R^2 - 2R(r_> - r_<) \cos\theta_>]^{1/2} \quad (14)$$

is the distance which the electron involved in $r_>$ would have from the other nucleus if $r_>$ were reduced to $r_> - r_<$; and

$$G = 1 + \cos\theta_1 \cos\theta_2 - \sin\theta_1 \sin\theta_2 \cos(\alpha_1 - \alpha_2), \quad (15)$$

α_1 and α_2 being the azimuthal angles of the two electrons, as shown in Fig. 1. The ambiguous signs in (12)

are to be interpreted independently for each of the three logarithmic terms as follows: both preceding the logarithm, and in the denominator, the upper (lower) sign is to be used if the quantity in absolute value signs in the numerator is positive (negative). [While one could write an expression identical in value to (12) without these ambiguous signs, it would be less convenient to evaluate for electronic positions on the internuclear line, as the fractions would reduce to $0/0$.]

IV. PROPERTIES AND LEGITIMACY OF THE SOLUTION

We must now convince ourselves that the expression (12) is a sufficiently good approximation to the ΔS defined by (7) to yield the correct asymptotic value of the integral in (5), with φ_1 substituted for Φ_1. Because of the exponential factor e^{-S_0} in φ_1, the integrand is appreciable only for small values of the distances ρ_1, ρ_2 of the two electrons from the internuclear line. For most z_1, z_2, $|z_1 + \frac{1}{2}R|$ and $|\frac{1}{2}R - z_2|$ are of order R, so the significant region is

$$\rho_1, \rho_2 \lesssim R^{1/2} \quad (16)$$

in atomic units. When either electron is near its nucleus the range is shortened from $O(R^{1/2})$ to $O(1)$.

For most positions of the electrons, the solution (12) is of order unity or less. It becomes large only when $r_< \gg R$ or when a numerator or denominator in one of the logarithmic expressions approaches zero. The former case corresponds to removing both electrons to a large distance, and reflects the fact that this double ionization costs more energy than for two isolated atoms. The only realizable divergences of the first two logarithms in (12) occur as electron 2 approaches the part of the z axis to the left of a in Fig. 1, or as electron 1 approaches the part to the right of b; for these cases our expression for $S_1 \to -\infty$, but the real S_1, computed with the truncated V', would be finite. The third logarithm diverges, giving $S_1 \to \infty$, when r_{12} approaches zero or approaches the "r_{12} shadow line" consisting of points along the path of integration ($r_{a1} - r_{b2} =$ constant, angles $=$ constant, $r_{a1} + r_{b2}$ increasing) beyond any point $r_{12} = 0$. In this region our neglect of the first two terms of (9) is not justified; the true ΔS will be small but nonzero
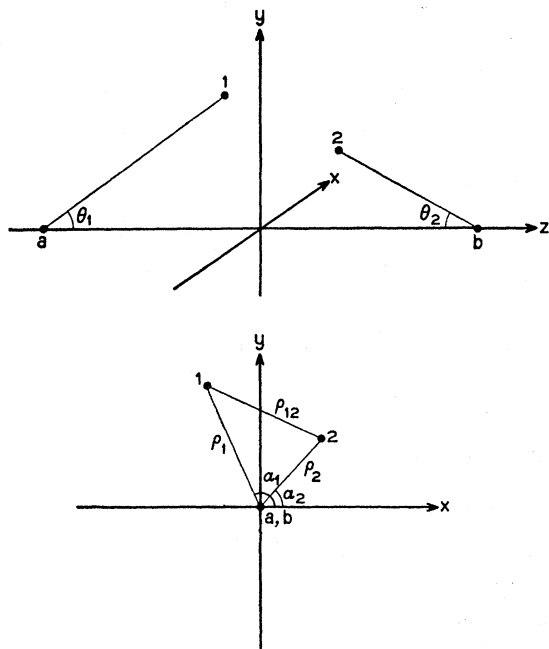

FIG. 1. Top: positions of protons a, b, and electrons 1, 2, with definitions of the polar angles. Bottom: projection of all positions on the x—y plane, showing azimuthal angles and projected distances ρ_1, ρ_2, ρ_{12}.

at $r_{12}=0$, and will rise somewhat as we pass further out along the r_{12} shadow line. Finally, our solution, although continuous across the hypersurface $r_{a1}=r_{b2}$, has a discontinuous third derivative on it. No serious consequences are to be expected from this weak discontinuity.

For an assessment of the importance of these defects in the region of interest to us, it will suffice to estimate the magnitude of the first two terms in (9), which we neglected in (10). On the provisional assumption that ΔS is well approximated by S_1, these two terms are $-\frac{1}{2}e^{S_1}\nabla^2 e^{-S_1}$. This is of order R^{-2} in all regions except where r_{12} is small. The corresponding correction to (10) can therefore only add terms of order R^{-1} to S_1, which are asymptotically negligible since in most of the region of interest S_1 is of order unity. When $r_{12} \to 0$, the numerator in the last logarithm of (12) contains terms of order r_{12} and smaller, the former always having a nonzero coefficient. For small r_{12} the denominator is of order R if the lower sign is to be used, and of order r_{12}^2/R if the upper sign is to be used. Thus in all cases the contribution to e^{-S_1} is of order $(r_{12}/R)^p$, where $p=(2G)^{-1/2}$ varies slowly with r_{a1} and r_{b2} and obeys $0 \le p \le \frac{1}{2}$. The singularity in $e^{S_1}\nabla^2 e^{-S_1}$ is therefore of order r_{12}^{-2}. This correction term to (10) is small compared with the term r_{12}^{-1} until r_{12} becomes of the order of a Bohr unit, and its integral gives a correction to S_1 of order r_{12}^{-1}, hence of order $R^{-1/2}$ over the region obeying (16).

We conclude, therefore, that it is legitimate to use (12) for the asymptotic evaluation of (5). However, the fractional error in the resulting J will be of order $R^{-1/2}$, and not, as stated by Gor'kov and Pitaevski,[4] of order R^{-1}.

V. EVALUATION OF THE INTEGRAL FOR J

We are now ready to evaluate the integral (5), using for Φ_1 the product of (8) and e^{-S_1}, where S_1 is given by (12). As the normal derivative of (8) on Σ is of order unity, while that of e^{-S_1} is of order R^{-1}, we can write

$$J \sim -\int_\Sigma d\mathbf{S} \cdot \exp(-S_0-S_1-PS_0-PS_1)$$
$$\times \nabla (r_{a1}+r_{b2}). \quad (17)$$

The integration is over the five variables x_1, y_1, x_2, y_2, and $2^{-1/2}(z_1+z_2)$, with the remaining coordinate $2^{-1/2} \times (z_1-z_2)$ fixed at zero. The contribution from $z=z_1 =z_2<-\frac{1}{2}R$ or $>\frac{1}{2}R$ (see Fig. 1) is of order Re^{-2R}, hence negligible in comparison with the main term, which as we shall see is of order $R^{5/2}e^{-2R}$. Thus we can limit z to the range between the two nuclei. Moreover, the range $\frac{1}{2}R-|z| \ll R$ gives a negligible contribution, so we may legitimately approximate r_{a1}, r_{b2}, and $\exp(-S_1-PS_1)$ in (17) by expressions valid for

$\rho_1, \rho_2 \ll r_{a1}, r_{b2}$. The resulting form of (17) is

$$J \sim -\frac{16R^2}{\pi^2}e^{-1-2R}\int_{-1/2R}^{1/2R} dz \iiiint dx_1 dy_1 dx_2 dy_2$$

$$\times \exp\left[-\frac{2R(\rho_1^2+\rho_2^2)}{R^2-4z^2}-\frac{2|z|}{R}\right]$$

$$\times \frac{\rho_{12}}{(R+2|z|)^2(R-2|z|)}, \quad (18)$$

where $\rho_{12}(=r_{12})$ is the distance of x_1, y_1 from x_2, y_2. The expression (18) coincides with the expression given by Gor'kov and Pitaevski,[4] after correction of an obvious typographical error in the latter.

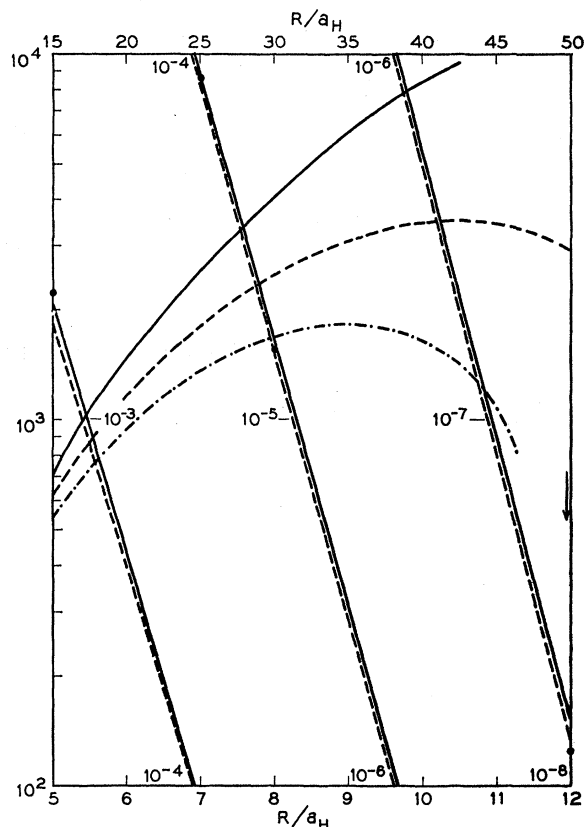Different choices are possible for the order of inte-

FIG. 2. Comparison of various expressions for $-J$ (one-half the singlet-triplet splitting) in atomic units (2 Ry). The steep curves show the dominant term, Eq. (19), of the exact asymptotic expression (upper curve), and the dominant term, Eq. (20), of the Heitler-London approximation (lower curve); the abscissas are to be read from the scale at the bottom, and the proper scale of ordinates for each portion of the diagram is marked on the curves. The individual points are the complete Heitler-London expression. The flatter curves show values of $-Je^{2R}$ for larger R, using the scale of ordinates at the left and the scale of abscissas at the top. Our Eq. (19) is again the top curve, Eq. (20) is the middle curve, and the complete Heitler-London expression is the bottom curve. The latter changes sign at $R=49.5a_H$, as indicated by the arrow.

gration in the multiple integral of (18). Our original procedure reduced (18) to a product of two integrals which had to be evaluated numerically. A simpler procedure, which gives the same numerical answer but requires only a single numerical integration, is to replace $dx_1 dy_1 dx_2 dy_2$ by $d^2\rho d^2\rho_{12}$, where $\rho = \frac{1}{2}(\rho_1 + \rho_2)$. The first four integrations can be done at once, and give, with $q = 1 - (2|z|/R)$,

$$J = -2\pi^{1/2} R^{5/2} e^{-2R} \int_0^1 e^{-q} q^{3/2} (2-q)^{1/2} dq + O(R^2 e^{-2R})$$

$$= -0.821 R^{5/2} e^{-2R} + O(R^2 e^{-2R}), \quad (19)$$

where we have now indicated the magnitude of the leading error term as discussed in Sec. IV. This J, it will be remembered, is $\frac{1}{2}(\mathcal{E}_g - \mathcal{E}_u)$ in atomic units (2 Ry). Gor'kov and Pitaevski[4] erroneously give a different integral expression from that in (19), and a numerical coefficient 1.47 instead of 0.821.

VI. CONCLUDING REMARKS

It is interesting to compare the value (19) with the leading term of the Heitler-London expression, which is[7]

$$J_{HL} = -[28/45 - (2/15)\gamma - (2/15)\ln R]R^3 e^{-2R}$$
$$+ O(R^2 e^{-2R}), \quad (20)$$

where γ is Euler's constant 0.5772. As has often been noted, this gives a physically impossible positive value at extremely large R, a defect which our expression (19)

---

[7] Y. Sugiura, Z. Physik **45**, 484 (1927). There is a numerical error in the formula quoted by Gor'kov and Pitaevski (Ref. 4).

rectifies. In the range of R for which the singlet-triplet splitting is of the order of hundredths to millionths of an electron volt, however, the two expressions are not greatly different. Figure 2 shows the comparison, and also the exact Heitler-London value, to show the magnitude of the neglected terms in (20).

The cause of the unreasonable behavior of the Heitler-London expression at very large R is that it is obtained from

$$J_{HL} = \int \int d^3\mathbf{r}_1 d^3\mathbf{r}_2 (P\Psi_{HL})(H - \mathcal{E}_0)\Psi_{HL}, \quad (21)$$

where Ψ_{HL} is the product (8) of single-atom functions ψ_a, ψ_b, and $\mathcal{E}_0$ is the ground-state energy of two isolated atoms. At large R this is dominated by the $1/r_{12}$ term in H, which gives as its contribution to J the self-energy of the charge distribution $\psi_a(\mathbf{r})\psi_b(\mathbf{r})$. For large R this is essentially a line charge, hence the logarithm in (20). To the accuracy we need, the correct J can also be written in a form similar to (20), with φ_1 replacing Ψ_{HL}. In this correct expression, however, no logarithmic term arises, because the mutual repulsion of the electrons make φ_1 small where r_{12} is small.

As we have noted in Sec. IV, the fractional error in the leading term of (19) is of order $R^{-1/2}$, rather than R^{-1} as in (20). This error arises from inaccuracy of our expression for the two-body wave function φ_1 in the region of small r_{12}. To obtain the next term, of order $R^2 e^{-2R}$, it would only be necessary to improve the wave function in this region, and this might well be much easier than to get the leading corrections to S_1 (of order R^{-1}) in a general region of space.