

Asymptotics of the exchange-splitting energy for a diatomic molecular ion from a volume-integral formula of symmetry-adapted perturbation theory

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The exchange-splitting energy J of the lowest *gerade* and *ungerade* states of the H_2^+ molecular ion was calculated using a volume integral expression of symmetry-adapted perturbation theory and standard basis set techniques of quantum chemistry. The performance of the proposed expression was compared to the well-known surface-integral formula. Both formulas involve the primitive function, which we calculated employing either the Hirschfelder-Silbey perturbation theory or the conventional Rayleigh-Schrödinger perturbation theory (the polarization expansion). Our calculations show that very accurate values of J can be obtained using the proposed volume-integral formula. When the Hirschfelder-Silbey primitive function is used in both formulas the volume formula gives much more accurate results than the surface-integral expression. We also show that using the volume-integral formula with the primitive function approximated by Rayleigh-Schrödinger perturbation theory, one correctly obtains only the first four terms in the asymptotic expansion of the exchange-splitting energy.

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I. INTRODUCTION

From the very advent of quantum chemistry, exchange energy has been one of the most prominent concepts of this scientific discipline [1]. It is especially important for theories of molecular binding and magnetism [2,3]. The hydrogen molecular ion, H_2^+ , is the simplest system for which exchange energy can be defined. In this case it is half of the difference between the energies of the lowest *gerade* and *ungerade* states:

$$J = \frac{1}{2}(E_g - E_u). \quad (1)$$

Being the simplest system with a chemical bond, H_2^+ is a very important model for more complex systems. It has served as a benchmark system for symmetry-adapted perturbation theories (SAPTs) (see, e.g., [4,5]). It was also proposed as a model of alkali-metal dimer cations [6].

Because the wave equation for H_2^+ separates in elliptic coordinates, many analytical results have been obtained for this system. Holstein and Herring [2,7] were the first to calculate the leading term, $-(2/e)Re^{-R}$, of the asymptotic expansion of J :

$$J(R) = 2e^{-R-1}R(j_0 + j_1 R^{-1} + j_2 R^{-2} + j_3 R^{-3} + \dots), \quad (2)$$

where R is the internuclear distance. Their approach relied on calculating J as a surface integral over the median plane M ,

$$J_{\text{surf}}[\phi] = \frac{-\int_M \phi \nabla \phi d\mathbf{S}}{\langle \phi | \phi \rangle - 2 \int_{\text{right}} \phi^2 dV}, \quad (3)$$

where ϕ is the so-called primitive function [8], which is defined later, and “right” denotes the half of the whole space to the right of the median plane (we use atomic units in this equation and throughout the paper). A similar calculation was included in Landau and Lifschitz’s textbook on quantum mechanics [9]. Bardsley *et al.* [10] used exponential parametrization of the

localized function ϕ and obtained two leading terms of J . The third term was calculated by Ovchinnikov and Sukhanov [11] by means of iterative solution of H_2^+ differential equations. Komarov and Slavyanov [12] and Damburg and Propin [13] used asymptotic solutions of the ordinary differential equations for the H_2^+ wave function and obtained four and nine leading terms of J , respectively. Brezin and Zinn-Justin [14] showed the connection between the leading term of J and the large- n form of van der Waals C_n coefficients of H_2^+ . Tang *et al.* [15] recovered the leading term of J by analytical summation to infinity of dominating terms of polarization theory. Such selective summation leads to the localized function ϕ of Herring and Holstein, as pointed out by Scott *et al.* [16].

The most complete results for H_2^+ were obtained by Čížek *et al.* [17], Graffi *et al.* [18], and Damburg *et al.* [19], who showed that the expansion of energy eigenvalues of H_2^+ in powers of $1/R$ is Borel summable for complex internuclear separations R . This Borel sum has a branch cut along the real R axis, and taking the limit of real R requires the addition of explicit imaginary “counter terms.” The imaginary part of the Borel sum determines the asymptotics of the van der Waals coefficients by a dispersion relation (this is a rigorous justification of Brezin and Zinn-Justin’s observation [14]). Čížek *et al.* [17] also gave formulas for the exponentially small terms and explicit numerical values of the first 52 j_k ’s of the expansion of Eq. (2).

Recently Burrows, Dalgarno, and Cohen [20] developed an algebraic perturbation theory, based on asymptotic solutions of H_2^+ differential equations and comparison technique. With their method they obtained the second, third, and fourth terms of (2) with relative errors of -2.8% , -17.8% , and 36.9% , respectively. Nevertheless, no previous work has succeeded in obtaining the expansion of Eq. (2), by means of standard *ab initio* approaches of quantum chemistry. As Whitton and Byers-Brown have pointed out [21], this is partly due to the fact that Rayleigh-Schrödinger (RS) perturbation theory must be summed to infinite order to yield the leading term of J .

The technique of Holstein and Herring was extended to the neutral H_2 molecule in the independent works of Gor’kov and

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Pitaevskii [22] and Herring and Flicker [23]. Extensions to many-electron systems were also provided [6,10,24–26].

In this communication we present a method of reproducing the asymptotic expansion of Eq. (2), using a volume-integral formula of SAPT. We apply our method to the H_2^+ ion to show its effectiveness for a system for which the exact solution is known [17–19]. Our procedure employs standard basis set techniques of electronic structure theory, therefore it generalizes straightforwardly to many-electron systems. It is now being applied in our group to the H_2 molecule, for which the validity of the results of Gor'kov and Pitaevskii [22] and of Herring and Flicker [23] has been questioned [27].

This paper is organized as follows: in Sec. II we recall the definition of the primitive function ϕ and derive the volume-integral formula for the exchange energy. Section III presents the approximations to ϕ that we use: the Hirschfelder-Silbey (HS) and RS perturbation theories. We describe the computational aspects of our study (basis sets, extrapolation, and fitting techniques) in Sec. IV. Section V contains the results of our investigation: the convergence with respect to the order of perturbation theory and with respect to the size of the basis set. Our article closes with concluding remarks in Sec. VI.

II. EXCHANGE ENERGY AND THE PRIMITIVE FUNCTION

The derivation of the surface-integral formula, (3), was given in Refs. [2,10]. Here we derive the volume-integral formula for J in terms of the primitive function ϕ . For an exhaustive analysis of the concept of primitive function we refer the reader to the paper by Kutzelnigg [8].

The primitive function ϕ is defined as a linear combination of the asymptotically degenerate *gerade* and *ungerade* wave functions, ψ_g and ψ_u ,

$$\phi = c_1 \psi_g + c_2 \psi_u, \quad (4)$$

which is localized on the nucleus a , in the sense that

$$\langle \phi_0 | P_{ab} \phi \rangle = o(R^{-n}) \quad (5)$$

for all $n > 0$, where $\phi_0 = 1s_a$ is the ground-state wave function of the hydrogen atom centered on nucleus a and P_{ab} is the operator of the reflection in the median plane of H_2^+ . Note that Kutzelnigg [8] used a more general definition and proposed the term *genuine primitive function* for the function satisfying condition (5). Since we use perturbation approximations to the primitive function, it is convenient to impose intermediate normalization:

$$\langle \phi_0 | \phi \rangle = 1. \quad (6)$$

Introducing the interaction energies \mathcal{E}_g and \mathcal{E}_u ,

$$\mathcal{E}_g = E_g - E_0, \quad \mathcal{E}_u = E_u - E_0, \quad (7)$$

with $E_0 = -\frac{1}{2}$ being the ground-state energy of the hydrogen atom, we may write the Schrödinger equation for the gerade and ungerade states as

$$\begin{aligned} (H_0 - E_0)\psi_g &= (\mathcal{E}_g - V)\psi_g, \\ (H_0 - E_0)\psi_u &= (\mathcal{E}_u - V)\psi_u. \end{aligned} \quad (8)$$

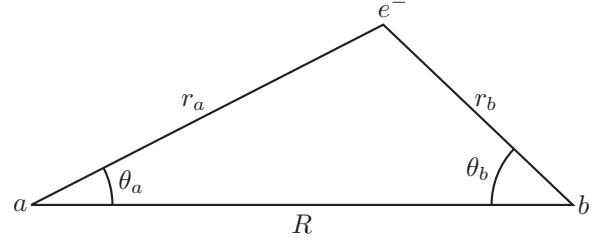


FIG. 1. Coordinates used in our study. Nuclei are denoted a and b .

The unperturbed Hamiltonian H_0 and the interaction operator V are

$$H_0 = -\frac{1}{2}\nabla^2 - \frac{1}{r_a}, \quad V = -\frac{1}{r_b} + \frac{1}{R}, \quad (9)$$

where r_a and r_b are the distances of the electron to the nuclei a and b , respectively.

Figure 1 shows the coordinates that we use. The wave functions ψ_g and ψ_u are expressed through ϕ as

$$c_1 \psi_g = A_g \phi, \quad c_2 \psi_u = A_u \phi, \quad (10)$$

where A_g and A_u are the symmetry projectors, defined as

$$A_g = \frac{1}{2}(1 + P_{ab}), \quad A_u = \frac{1}{2}(1 - P_{ab}). \quad (11)$$

After inserting formulas (10) into (8) and taking inner products with ϕ_0 , one obtains

$$\begin{aligned} \mathcal{E}_g \langle \phi_0 | (1 + P_{ab}) \phi \rangle &= \langle \phi_0 | V (1 + P_{ab}) \phi \rangle, \\ \mathcal{E}_u \langle \phi_0 | (1 - P_{ab}) \phi \rangle &= \langle \phi_0 | V (1 - P_{ab}) \phi \rangle. \end{aligned} \quad (12)$$

The solution for $J = \frac{1}{2}(\mathcal{E}_g - \mathcal{E}_u) = \frac{1}{2}(E_g - E_u)$ is

$$J_{\text{SAPT}}[\phi] = \frac{\langle \phi_0 | V P_{ab} \phi \rangle - \langle \phi_0 | V \phi \rangle \langle \phi_0 | P_{ab} \phi \rangle}{1 - \langle \phi_0 | P_{ab} \phi \rangle^2}. \quad (13)$$

Note that this expression for J contains only volume integrals and does not involve cancellation of long-range terms—both parts of the numerator decay exponentially, in accordance with (5)—so that this expression can be used for very large R without loss of significant figures. When the primitive function ϕ is expanded in powers of V , Eq. (13) generates the expansions of the exchange energy appearing in SAPT [28–30]. We refer to Eq. (13) as the *volume-integral formula* or the SAPT formula for the exchange energy.

III. APPROXIMATIONS TO THE PRIMITIVE FUNCTION

In principle, ϕ could be obtained as a combination of variationally calculated ψ_g and ψ_u in appropriate bases. This would, however, quickly lead to a loss of accuracy for large R . We therefore decided to test other approximations to ϕ , which can be obtained directly, without knowledge of ψ_g and ψ_u .

The HS perturbation theory [31] is constructed to provide a perturbation expansion of the primitive function in orders of the perturbation V

$$\phi = \phi_{\text{HS}}^{(0)} + \phi_{\text{HS}}^{(1)} + \phi_{\text{HS}}^{(2)} + \dots \quad (14)$$

It converges to the results of variational calculations with the same basis set, provided that this basis set is invariant under

symmetry operations [32]. The equations for the consecutive corrections $\phi_{\text{HS}}^{(n)}$ to the HS wave function are [32]

$$\begin{aligned} \phi_{\text{HS}}^{(n)} = & -R_0 V \phi_{\text{HS}}^{(n-1)} + \sum_{k=1}^n E_g^{(k)} R_0 A_g \phi_{\text{HS}}^{(n-k)} \\ & + \sum_{k=1}^n E_u^{(k)} R_0 A_u \phi_{\text{HS}}^{(n-k)}, \end{aligned} \quad (15)$$

where the energy corrections $E_g^{(n)}$ and $E_u^{(n)}$ are given by

$$\begin{aligned} E_v^{(n)} = & \langle \phi_0 | A_v \phi_0 \rangle^{-1} \left(\langle \phi_0 | V A_v \phi_{\text{HS}}^{(n-1)} \rangle \right. \\ & \left. - \sum_{k=1}^{n-1} E_v^{(k)} \langle \phi_0 | A_v \phi_{\text{HS}}^{(n-k)} \rangle \right), \quad v = g, u. \end{aligned} \quad (16)$$

The zeroth-order wave function and energy are those of the unperturbed hydrogen atom, $\phi_{\text{HS}}^{(0)} = \phi_0 \equiv 1s_a$. The resolvent R_0 is defined by

$$R_0 = (H_0 - E_0 + P_0)^{-1} (1 - P_0), \quad (17)$$

where $P_0 = |\phi_0\rangle\langle\phi_0|$ is the operator projecting on the unperturbed wave function.

The standard RS perturbation theory applied to molecular interactions with H_0 and V defined as in Eq. (9) is known as the polarization expansion or polarization approximation [33]. It gives in finite order a good approximation to the primitive function. Strictly speaking, the polarization approximation gives an asymptotic representation of the primitive function in the following sense [34]:

$$\phi = \sum_{k=0}^n \phi_{\text{RS}}^{(k)} + O(R^{-\kappa(n+1)}), \quad (18)$$

with $\kappa = 2$ when at least one of the interacting subsystems has a net charge and $\kappa = 3$ otherwise. The wave-function corrections in this theory, $\phi_{\text{RS}}^{(n)}$, are defined recursively by

$$\phi_{\text{RS}}^{(n)} = -R_0 V \phi_{\text{RS}}^{(n-1)} + \sum_{k=1}^n E_{\text{RS}}^{(k)} R_0 \phi_{\text{RS}}^{(n-k)}, \quad (19)$$

and the energy corrections $E_{\text{RS}}^{(n)}$ are calculated as $E_{\text{RS}}^{(n)} = \langle \phi_0 | V \phi_{\text{RS}}^{(n-1)} \rangle$. The unperturbed wave function and reduced resolvent are the same as in the HS theory.

IV. COMPUTATIONAL ASPECTS

The basis set used by us consists of functions

$$\chi_c^{N,M} = C_{N,M} e^{-r_c} L_N^{2M+2}(2r_c) r_c^M P_M(\cos \theta_c), \quad (20)$$

where $c = a, b$ and $L_N^{2M+2}(x)$ and $P_M(x)$ are the generalized Laguerre and Legendre polynomials, respectively, defined as in, e.g., Ref. [35]. The normalization constant of the basis function $\chi_c^{N,M}$ is denoted $C_{N,M}$. The angles θ_a and θ_b are the interior ones of the triangle given by r_a , r_b , and R (see Fig. 1), so that $\theta_b = P_{ab}\theta_a$ and $\chi_b^{N,M} = P_{ab}\chi_a^{N,M}$. This convention for θ_b was used by Bardsley *et al.* in Ref. [10]. Two-center integrals generated when using this basis set are easily calculated using the conventional elliptic coordinates

$\xi = (r_a + r_b)/R$ and $\eta = (r_a - r_b)/R$. The unperturbed wave function is explicitly included in the basis, $\phi_0 = \chi_a^{0,0}$.

Basis functions centered on the same nucleus are orthonormal, whereas overlap integrals of functions centered on different atoms decay exponentially:

$$\langle \chi_a^{N_1, M_1} | \chi_b^{N_2, M_2} \rangle \sim e^{-R}. \quad (21)$$

This reduces linear dependencies in the basis set at large R , allowing for accurate calculations of the asymptotic constants j_k . The values of N and M are the same for basis functions centered on nuclei a and b , therefore basis (20) is invariant under the action of P_{ab} , and converged HS theory gives results exact in this basis [32]. We introduce a hierarchy of basis sets through the parameter Ω constraining N and M :

$$N + M \leq \Omega. \quad (22)$$

This hierarchy is useful for making extrapolations to the complete basis set limit. N and M are treated symmetrically in Eq. (22) in order to maintain consistency with the multipole expansion of the wave function and to provide the best convergence at large R .

The basis set of Eq. (20) is appropriate for large internuclear distances R but is inadequate for small ones because of the strong linear dependencies appearing at larger values of Ω . We decided that the smallest internuclear distance used in the fitting of the asymptotic constants j_k is $R = 60$. For this distance the octupole precision (exact to 64 significant decimal digits) was required to perform accurate calculations for $\Omega = 25$ (702 basis functions).

Chipman and Hirschfelder used a basis similar to (20), but with monomials in r_a and r_b instead of Laguerre polynomials, when they applied different perturbation theories to H_2^+ [4]. The basis (20) restricted to functions centered on the nucleus a was used by Coulson [36] and by Morgan and Simon [37] in their calculations of van der Waals coefficients of H_2^+ .

The regularity of the Ω dependence of the computed values of J permits efficient application of the extrapolation technique to accelerate basis set convergence. We used Levin's u transformation of the form [38]

$$U_n = \frac{\sum_{i=0}^n (-1)^i \binom{n}{i} (i+1)^{n-2} Z_i A_i^{-1}}{\sum_{i=0}^n (-1)^i \binom{n}{i} (i+1)^{n-2} A_i^{-1}}, \quad (23)$$

where U_n is the resulting accelerated sequence, and $Z_i = A_0 + A_1 + \dots + A_i$ is the partial sum to be accelerated. The Levin u transformation is considered to be the best general-purpose convergence accelerating sequence transformation [39]. For an efficient and numerically stable algorithm and general discussion of this and similar transformations, see Ref. [40].

In the case of basis extrapolation there are many possible choices of A_i and Z_i . After extensive analysis of the performance of different choices we decided to report results obtained with the six-term Levin u transformation applied to the six best basis sets. With this choice we have $Z_n = J(\Omega = n + 20)$, $A_0 = J(\Omega = 20)$, and $A_n = J(\Omega = n + 20) - J(\Omega = n + 19)$ for $n > 0$.

We used the least-squares method to extract the asymptotic constants j_k from the calculated values of $J(R)$. In order to increase the numerical stability of our analysis, we scaled the values of $J(R)$, multiplying them by $e^{R+1}/(2R)$ prior to the

fitting procedure. The fitting functions were then polynomials in R^{-1} , in accordance with Eq. (2):

$$f(R) = \sum_{i=0}^L \frac{\tilde{j}_i}{R^i}. \quad (24)$$

It is important to choose the appropriate degree of the fitting polynomial L . A fit with a too small L would fail to extract all the available information from the calculated values, while a too large L would lead to inaccurate results.

In our calculations we used a grid of 46 equally spaced values of internuclear distance $R = 60, 62, \dots, 150$ in the fitting procedure. We used an additional “test set” of nine internuclear distances, $R = 65, 75, \dots, 145$, to assess the quality of fits. Analysis of the errors given by fits with different L values for the nine points in the test set allowed us to determine the optimal values of L . We found that for $\Omega = 25$ the optimal value of L is 10 when the volume-integral formula is used. For the surface-integral expression the optimal choice of L is 5.

V. RESULTS AND DISCUSSION

A. Convergence of perturbation theory

When the primitive function is approximated by either ϕ_{HS} or ϕ_{RS} , the exchange energy J can be expanded in powers of V ,

$$J = \sum_{k=1}^{\infty} J_{\text{SAPT}}^{(k)}[\phi], \quad (25)$$

and the corrections $J_{\text{SAPT}}^{(n)}[\phi]$ are given by

$$J_{\text{SAPT}}^{(n)}[\phi] = \langle \phi_0 | V P_{ab} \phi^{(n-1)} \rangle - \sum_{k=0}^{n-1} \langle \phi_0 | V \phi^{(k)} \rangle \langle \phi_0 | P_{ab} \phi^{(n-k-1)} \rangle + O(e^{-2R}), \quad (26)$$

where ϕ stands for either ϕ_{HS} or ϕ_{RS} .

The HS perturbation theory is characterized by very good convergence [32,41]. We observed that the convergence radius for the series of exchange corrections $J_{\text{SAPT}}^{(n)}[\phi_{\text{HS}}]$ was close to 2 and was almost independent of the internuclear distance R . These convergence properties result in a similarly good convergence of the asymptotic coefficients j_k of Eq. (2) fitted to the results of calculations for finite R . Figure 2 demonstrates the convergence of j_k 's obtained from the HS theory.

In comparison to the HS theory, the convergence properties of the RS perturbation expansion are much more complicated [42]. This is reflected in the convergence of the exchange-energy corrections $J_{\text{SAPT}}^{(n)}[\phi_{\text{RS}}]$ calculated from Eq. (26). These corrections are identical to those of the symmetrized RS (SRS) perturbation theory [43]. For perturbation orders n larger than 10 and smaller than some critical value n_{crit} , the ratios of exchange-energy corrections $J_{\text{SAPT}}^{(n+1)}[\phi_{\text{RS}}]/J_{\text{SAPT}}^{(n)}[\phi_{\text{RS}}]$ are approximately equal to 0.5. For n larger than n_{crit} these ratios are close to 1. The value of n_{crit} increases with the internuclear distance R . This is illustrated in Fig. 3.

It is clear that the convergence properties of the series of corrections $J_{\text{SAPT}}^{(n)}[\phi_{\text{RS}}]$ are pathological and it is not possible

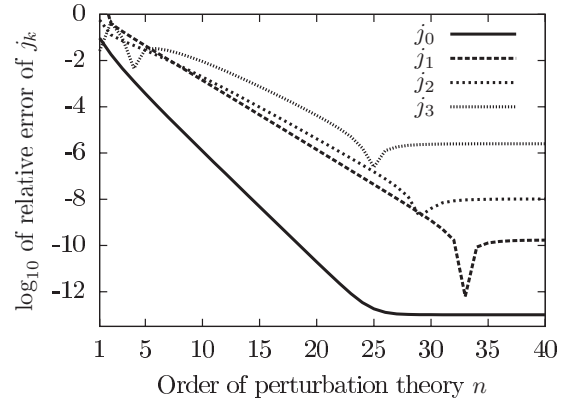


FIG. 2. Convergence of j_0 , j_1 , j_2 , and j_3 as a function of the perturbation order n of the Hirschfelder-Silbey perturbation theory. Volume-integral formula and basis set $\Omega = 25$ were used. Errors are calculated with respect to the exact values given in Ref. [17]. Errors remaining beyond the 30th order are due to the basis set incompleteness.

to obtain the exact limit of the series, (26), with $\phi = \phi_{\text{RS}}$ through direct summation. The practical limit is obtained when corrections are summed up to n_{crit} . This method of summation gives very accurate values of $J(R)$, and the figure illustrating the convergence of the fitted asymptotic constants j_k , $k = 0, 1, 2, 3$, would be practically indistinguishable from Fig. 2 illustrating the convergence of the HS theory.

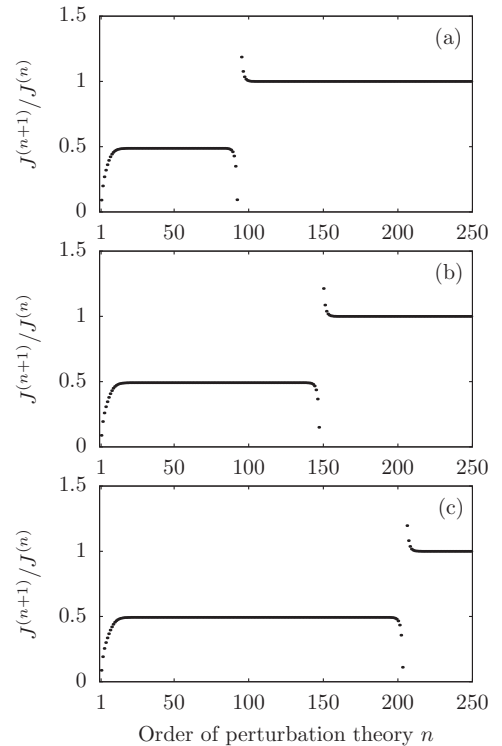


FIG. 3. Fractions of subsequent corrections to the exchange energy $J_{\text{SAPT}}^{(n)}[\phi_{\text{RS}}]$ for three internuclear distances: (a) $R = 40$, (b) $R = 60$, and (c) $R = 80$. Basis set $\Omega = 25$ was used.

We calculated the convergence radius ρ of the series of corrections $\phi_{\text{RS}}^{(n)}$ and found that it is always greater than 1 but only marginally at large R . This convergence radius is determined [42] by a pair of branch points of the two lowest lying eigenvalues of the non-Hermitian operator $H_0 + \zeta V$, where ζ is a complex scaling parameter. The radius ρ can be written in the form $1 + \gamma$, with $\gamma \sim e^{-2R}$ (for instance, $\gamma = 1.84 \times 10^{-47}$ for $R = 60$ and $\gamma = 1.90 \times 10^{-124}$ for $R = 150$). The physical value of the scaling parameter, $\zeta = 1$, therefore lies inside the convergence circle of the $\phi_{\text{RS}}^{(n)}$ series. Thus, the series of exchange corrections $J_{\text{RS}}^{(n)}$ must converge despite the

apparent stabilization of the high-order terms. Since the sum of corrections $\phi_{\text{RS}}^{(n)}$ satisfies the Schrödinger equation the polarization series converges to the exact, gerade wave function of H_2^+ satisfying $P_{ab}\phi_{\text{RS}} = \phi_{\text{RS}}$ in the limit $n \rightarrow \infty$. Thus, in view of the symmetry condition $P_{ab}\phi_{\text{RS}} = \phi_{\text{RS}}$, the volume-integral formula, (13), exhibits 0/0 singularity at $n \rightarrow \infty$.

We now show that this singularity is removable. Our derivation is based on the ideas given in Ref. [44]. The limit of the series of Eq. (25) with $\phi = \phi_{\text{RS}}$ can be obtained from the limit $\zeta \rightarrow 1$ in Eq. (13) in which V and ϕ are replaced by ζV and $\phi_{\text{RS}}(\zeta)$, respectively:

$$J_{\text{SAPT}}[\phi_{\text{RS}}] = \lim_{\zeta \rightarrow 1} \frac{\langle \phi_0 | \zeta V P_{ab} \phi_{\text{RS}}(\zeta) \rangle \langle \phi_0 | \phi_{\text{RS}}(\zeta) \rangle - \langle \phi_0 | \zeta V \phi_{\text{RS}}(\zeta) \rangle \langle \phi_0 | P_{ab} \phi_{\text{RS}}(\zeta) \rangle}{\langle \phi_0 | \phi_{\text{RS}}(\zeta) \rangle^2 - \langle \phi_0 | P_{ab} \phi_{\text{RS}}(\zeta) \rangle^2}. \quad (27)$$

Note that we use here a slight modification of the volume-integral formula, (13), which is independent of the normalization of ϕ . The limit in Eq. (27) can be obtained with the use of the l'Hospital rule. The derivative of the numerator \mathcal{N} on the left-hand side of Eq. (27) is

$$\left. \frac{d\mathcal{N}}{d\zeta} \right|_{\zeta=1} = \langle \phi_0 | V \psi_g \rangle \langle \phi_0 | (1 - P_{ab}) \psi^{(1)} \rangle - \langle \phi_0 | V (1 - P_{ab}) \psi^{(1)} \rangle \langle \phi_0 | \psi_g \rangle, \quad (28)$$

where $\psi^{(1)}$ is the derivative of $\phi_{\text{RS}}(\zeta)$ with respect to ζ at $\zeta = 1$,

$$\psi^{(1)} = \left. \frac{d\phi_{\text{RS}}}{d\zeta} \right|_{\zeta=1} = - \sum_{s \neq g} \frac{\langle \psi_s | V \psi_g \rangle}{E_s - E_g} \psi_s, \quad (29)$$

where the summation involves all excited states s of H (the energy and wave function of an excited state s are denoted E_s and ψ_s , respectively). Equation (28) can be rearranged to yield

$$\left. \frac{d\mathcal{N}}{d\zeta} \right|_{\zeta=1} = \langle \phi_0 | \psi_g \rangle \langle \phi_0 | (P_{ab} - 1)(H - E_g) \psi^{(1)} \rangle = \langle \phi_0 | \psi_g \rangle \langle \phi_0 | (1 - P_{ab}) V \psi_g \rangle. \quad (30)$$

The ζ derivative of the denominator \mathcal{D} of Eq. (27) reads

$$\left. \frac{d\mathcal{D}}{d\zeta} \right|_{\zeta=1} = 2 \langle \phi_0 | \psi_g \rangle \langle \phi_0 | (1 - P_{ab}) \psi^{(1)} \rangle. \quad (31)$$

The contribution of ψ_u dominates in Eq. (29), therefore

$$\left. \frac{d\mathcal{D}}{d\zeta} \right|_{\zeta=1} = \frac{\langle \phi_0 | \psi_g \rangle}{J} [2 \langle \phi_0 | \psi_u \rangle \langle \psi_u | V \psi_g \rangle + O(e^{-R})]. \quad (32)$$

Consequently, the limit of Eq. (27) is

$$J_{\text{SAPT}}[\phi_{\text{RS}}] = J \frac{\langle \phi_0 | (1 - P_{ab}) V \psi_g \rangle}{2 \langle \phi_0 | \psi_u \rangle \langle \psi_u | V \psi_g \rangle} + O(e^{-2R}). \quad (33)$$

Expressing ψ_g and ψ_u via the primitive function ϕ , we find

$$J_{\text{SAPT}}[\phi_{\text{RS}}] = J \langle \phi | \phi \rangle \frac{\langle (1 - P_{ab}) \phi | V (1 + P_{ab}) \phi \rangle}{\langle (1 - P_{ab}) \phi | V (1 + P_{ab}) \phi \rangle} + O(J^2). \quad (34)$$

The SRS perturbation theory is therefore convergent, although it gives a limit different from the true value of the exchange

energy. This limit is nevertheless asymptotically exact: when the primitive function ϕ in Eq. (34) is approximated using the multipole expansion [34], one obtains the expression

$$\frac{J_{\text{SAPT}}[\phi_{\text{RS}}]}{J} = 1 + \frac{w_4}{R^4} + \frac{w_5}{R^5} + \frac{w_6}{R^6} + \frac{w_7}{R^7} + O(R^{-8}), \quad (35)$$

with $w_4 = w_5 = 67/8$, $w_6 = 173/4$, and $w_7 = 14\,657/32$. The numerical results given in Sec. V C confirm this asymptotic behavior of the SRS exchange energy.

When a very similar reasoning is applied to the removable singularity of $J_{\text{surf}}[\phi_{\text{RS}}]$, one obtains

$$\frac{J_{\text{surf}}[\phi_{\text{RS}}]}{J} = 1 + O(e^{-R}), \quad (36)$$

in agreement with the conclusions in Ref. [45].

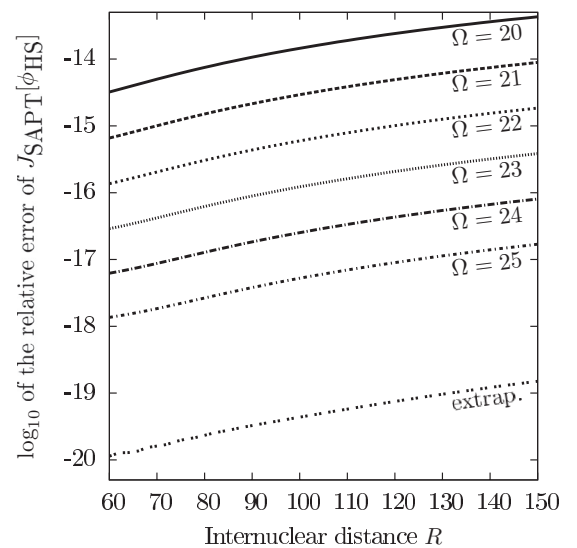


FIG. 4. Decimal logarithms of errors of $J_{\text{SAPT}}^{(n)}[\phi_{\text{HS}}]$ and values extrapolated from the six best bases: $\Omega = 20, \dots, 25$. Errors are calculated with respect to exact results of Čížek et al. [17].

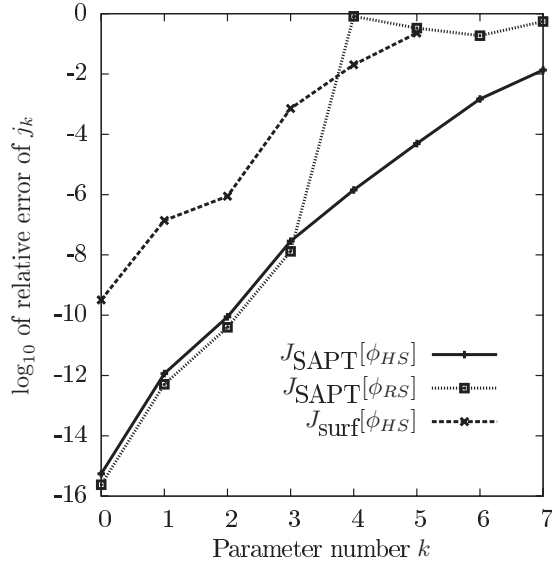


FIG. 5. Decimal logarithms of errors of j_k , $k = 0, \dots, 7$, obtained with the primitive functions ϕ_{HS} and ϕ_{RS} . Results extrapolated from basis sets $\Omega = 20, 21, \dots, 25$.

B. Basis set convergence

We found that the convergence of results with respect to Ω is very regular for a wide range of internuclear distances. When Ω is increased by 3, the relative errors of exchange energy (compared to exact results of Čížek *et al.* [17]) decrease by two orders of magnitude. This behavior is shown in Fig. 4.

Figure 4 also shows that this good convergence can be further improved by the application of the Levin u transformation. When this transformation is applied to the results calculated in basis sets $\Omega = 17, 18, \dots, 22$, one obtains exchange energy with the accuracy almost identical to that of $\Omega = 25$. Therefore it can be estimated that values computed as the transformation of six energies, $J(\Omega = 20), \dots, J(\Omega = 25)$, are of an accuracy similar to that possible to calculate with basis $\Omega = 28$ (bases $\Omega = 25$ and $\Omega = 28$ contain 702 and 870 basis functions, respectively).

C. Comparison of numerical results obtained from the volume- and surface-integral formulas

In Fig. 5 we show the errors of the asymptotic expansion parameters j_k for the two considered approximations to the

primitive function ϕ . These parameters are also listed in Table I.

It can be seen that the volume-integral formula with ϕ_{HS} is able to reproduce all j_k of Eq. (2), provided a sufficient basis set and numerical precision are used. It is also clear from Fig. 5 that the SRS theory is able to reproduce only four leading coefficients of the asymptotic expansion, (2).

We found by least-squares fitting that the relative error of the SRS exchange energy with respect to the HS one is well represented by a polynomial in $1/R$,

$$\frac{J_{SAPT}[\phi_{RS}]}{J_{SAPT}[\phi_{HS}]} = 1 + \frac{\tilde{w}_4}{R^4} + \frac{\tilde{w}_5}{R^5} + \frac{\tilde{w}_6}{R^6} + \frac{\tilde{w}_7}{R^7} + \dots, \quad (37)$$

with $\tilde{w}_4 = 8.375 \pm 5 \times 10^{-15}$, $\tilde{w}_5 = 8.375 \pm 6 \times 10^{-12}$, $\tilde{w}_6 = 43.25 \pm 4 \times 10^{-9}$, and $\tilde{w}_7 = 458.031 \pm 1 \times 10^{-6}$. The values obtained by fitting are in perfect agreement with the ones calculated from Eq. (34).

Somewhat surprisingly, we found that ϕ_{HS} and ϕ_{RS} give practically identical results (up to more than 20 digits) when used in the surface-integral formula, (3). For instance, when $R = 100$ and $\Omega = 25$ we obtained $J_{surf}[\phi_{HS}] = J_{surf}[\phi_{RS}] = -2.749\,901\,239\,50 \times 10^{-42}$, while the exact value is $J_{exact} = -2.749\,901\,239\,63 \times 10^{-42}$. The errors of these approximate values are, however, much larger than those obtained with the volume integral and the HS primitive function. We found that the relative errors of $J_{SAPT}[\phi_{HS}]$, defined as $\Delta J = |(J - J_{exact})/J_{exact}|$, are of the order of 10^{-17} , while the relative errors of $J_{surf}[\phi_{HS}] = J_{surf}[\phi_{RS}]$ range from 10^{-13} to 10^{-9} for R between 60 and 150 (the values of J_{exact} are calculated from the exact asymptotic constants [17]). The errors of $J_{SAPT}[\phi_{RS}]$ are of the order of 10^{-6} to 10^{-8} in this range of distances. These increased errors (compared to those of $J_{SAPT}[\phi_{HS}]$) are not related to a remaining basis set incompleteness but are caused by the incorrect values of the higher j_k coefficients predicted by $J_{SAPT}[\phi_{RS}]$.

The higher errors resulting from using the surface-integral formula can be understood when the quality of the wave function is considered. The accuracy of $J_{surf}[\phi]$ depends mainly on the accuracy of the wave function ϕ in the vicinity of the median plane M . We can inspect the quality of any approximate wave function ψ by analyzing the local energy associated with this wave function:

$$E_{loc}(\mathbf{r}) = \frac{H\psi(\mathbf{r})}{\psi(\mathbf{r})}. \quad (38)$$

TABLE I. Values of j_k obtained from different approximations and the exact values calculated by Čížek *et al.* [17]. The degrees of the fitting polynomials were 8 for J_{SAPT} and 4 for J_{surf} . The values extrapolated from the six best basis sets ($\Omega = 20, \dots, 25$) were used in the fits.

	J_{exact}	$J_{SAPT}[\phi_{HS}]$	$J_{SAPT}[\phi_{RS}]$	$J_{surf}[\phi_{HS}]$
j_0	-1	-0.999 999 999 999 999 45	-0.999 999 999 999 999 76	-0.999 999 999 998
j_1	-0.5	-0.500 000 000 000 000 58	-0.500 000 000 000 000 26	-0.500 000 069
j_2	3.125	3.125 000 000 000 28	3.125 000 000 000 12	3.124 997 2
j_3	2.729 166 67	2.729 166 59	2.729 166 63	2.731 1
j_4	10.216 146	10.216 160	1.8	10.01
j_5	37.864 3	37.862 5	25.0	47.0
j_6	113.26	113.43	92.0	—
j_7	789.2	778.5	353.0	—

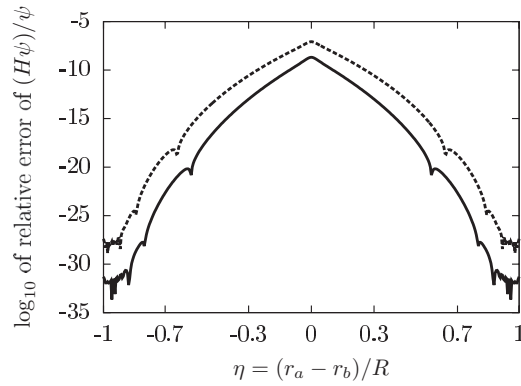


FIG. 6. Errors of the local energy $(H\psi)/\psi$ for $\psi = (1 + P_{ab})\phi_{\text{HS}}$ calculated for the line joining the nuclei ($\xi = 1$, $\eta = -1, \dots, 1$). Internuclear distance $R = 100$; basis sets $\Omega = 20$ (dashed line) and $\Omega = 25$ (solid line).

The local energy was used in a similar context by Bartlett, who applied it to assess the quality of his numerical approximation to the wave function of the helium atom in Ref. [46].

Figure 6 shows the errors of E_{loc} for the line joining the nuclei. The reference energy was calculated as the sum of $E_g^{(n)}(\text{HS})$ up to $n = 150$. This graph presents E_{loc} for the symmetrized ϕ_{HS} function, $\psi = (1 + P_{ab})\phi_{\text{HS}}$, obtained with the $\Omega = 25$ basis set. The graph for ϕ_{RS} is not given, as it would be indistinguishable from the one for ϕ_{HS} with this scale. It can be seen that the primitive functions investigated in our work give a very good description of the part of configuration space close to the nuclei but have much larger errors at the median plane, i.e., in the region relevant for the accuracy of the surface-integral formula.

VI. CONCLUSIONS

We have found that the SAPT volume-integral formula proposed by us gives very accurate values of the exchange-splitting energy when the primitive function is approximated either by the HS or by the RS perturbation theory. This volume-integral formula exhibits much superior basis set convergence than the conventional surface-integral expression of Herring and Holstein. This is due to the fact that the accuracy of the latter depends on the quality of the wave function at the median plane, i.e., far from the nuclei. The very good (and very similar) basis set convergence of $J_{\text{SAPT}}[\phi_{\text{HS}}]$ and $J_{\text{SAPT}}[\phi_{\text{RS}}]$ can be further improved by extrapolation techniques such as the Levin u transformation. It has also been found that the values of the asymptotic constants obtained from $J_{\text{surf}}[\phi_{\text{HS}}]$ and $J_{\text{surf}}[\phi_{\text{RS}}]$ are identical.

It is remarkable that the perturbation expansion of $J_{\text{SAPT}}[\phi_{\text{RS}}]$, which is equivalent to the SRS perturbation theory, does converge but gives accurately only the first four terms of the asymptotic expansion of Eq. (2). The unphysical values of further terms are due to the removable $0/0$ singularity of $J_{\text{SAPT}}[\phi_{\text{RS}}]$ in the limit $n \rightarrow \infty$.

It should be pointed out that application of the proposed volume-integral formula involves standard basis set and integral evaluation techniques of quantum chemistry and therefore this formula can be more easily applied in the case of many-electron systems, both ionic and neutral, than the surface-integral expression.

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- [1] W. Heitler and F. London, *Z. Phys.* **44**, 455 (1927).
- [2] C. Herring, *Rev. Mod. Phys.* **34**, 631 (1962).
- [3] C. Herring, in *Magnetism: A Treatise on Modern Theory and Materials*, Vol. IV, edited by G. Rado and H. Suhl (Academic Press, New York, 1966).
- [4] D. M. Chipman and J. O. Hirschfelder, *J. Chem. Phys.* **59**, 2838 (1973).
- [5] B. Jeziorski and W. Kołos, *Int. J. Quant. Chem.* **12**(Suppl. 1), 91 (1977).
- [6] T. C. Scott, M. Aubert-Frécon, G. Hadinger, D. Andrae, J. Grotendorst, and J. D. Morgan, III, *J. Phys. B* **37**, 4451 (2004).
- [7] T. Holstein, *J. Phys. Chem.* **56**, 832 (1952).
- [8] W. Kutzelnigg, *J. Chem. Phys.* **73**, 343 (1980).
- [9] L. Landau and E. M. Lifshitz, *Quantum Mechanics: Non-Relativistic Theory* (Pergamon Press, Oxford, UK, 1965) p. 291.
- [10] J. N. Bardsley, T. Holstein, B. R. Junker, and S. Sinha, *Phys. Rev. A* **11**, 1911 (1975).
- [11] A. A. Ovchinnikov and A. D. Sukhanov, *Sov. Phys. Dokl.* **9**, 685 (1965).
- [12] I. V. Komarov and S. Yu. Slavyanov, *ZhETF* **52**, 1368 (1967) [*JETP* **25**, 910 (1967)].
- [13] R. J. Damburg and R. Kh. Propin, *J. Phys. B* **1**, 681 (1968).
- [14] E. Brezin and J. Zinn-Justin, *J. Phys. Lett.* **40**, 511 (1979).
- [15] K. T. Tang, J. P. Toennies, and C. L. Yiu, *J. Chem. Phys.* **94**, 7266 (1991).
- [16] T. C. Scott, A. Dalgarno, and J. D. Morgan, III, *Phys. Rev. Lett.* **67**, 1419 (1991).
- [17] J. Čížek, R. J. Damburg, S. Graffi, V. Grecchi, E. M. Harrell, II, J. G. Harris, S. Nakai, J. Paldus, R. Kh. Propin, and H. J. Silverstone, *Phys. Rev. A* **33**, 12 (1986).
- [18] S. Graffi, V. Grecchi, E. M. Harrell II, and H. J. Silverstone, *Ann. Phys. (NY)* **165**, 441 (1985).
- [19] R. J. Damburg, R. Kh. Propin, S. Graffi, V. Grecchi, E. M. Harrell, II, J. Čížek, J. Paldus, and H. J. Silverstone, *Phys. Rev. Lett.* **52**, 1112 (1984).
- [20] B. L. Burrows, A. Dalgarno, and M. Cohen, *Phys. Rev. A* **81**, 042508 (2010).
- [21] W. N. Whitton and W. Byers-Brown, *Int. J. Quant. Chem.* **10**, 71 (1976).
- [22] L. P. Gor'kov and L. P. Pitaevskii, *Sov. Phys. Dokl.* **8**, 788 (1964).

- [23] C. Herring and M. Flicker, *Phys. Rev.* **134**, A362 (1964).
- [24] B. M. Smirnov and M. I. Chibisov, *ZhETF* **48**, 939 (1965) [*JETP* **21**, 624 (1965)].
- [25] K. T. Tang, J. P. Toennies, M. Wanschura, and C. L. Yiu, *Phys. Rev. A* **46**, 3746 (1992).
- [26] M. J. Jamieson, A. Dalgarno, M. Aymar, and J. Tharmel, *J. Phys. B* **42**, 095203 (2009).
- [27] B. L. Burrows, A. Dalgarno, and M. Cohen, *Phys. Rev. A* **86**, 052525 (2012).
- [28] B. Jeziorski, R. Moszyński, and K. Szalewicz, *Chem. Rev.* **94**, 1887 (1994).
- [29] K. Szalewicz, K. Patkowski, and B. Jeziorski, in *Intermolecular Forces and Clusters (Structure and Bonding, Vol. 116)*, edited by D. J. Wales (Springer-Verlag, Heidelberg, 2005), pp. 43–117.
- [30] R. Moszyński, in *Challenges and Advances in Computational Chemistry and Physics*, Vol. 4, edited by A. W. Sokalski (Springer, Dordrecht, 2007), pp. 1–152.
- [31] J. O. Hirschfelder and R. Silbey, *J. Chem. Phys.* **45**, 2188 (1966).
- [32] G. Chałasiński, B. Jeziorski, and K. Szalewicz, *Int. J. Quant. Chem.* **11**, 247 (1977).
- [33] J. O. Hirschfelder, *Chem. Phys. Lett.* **1**, 325 (1967).
- [34] B. Jeziorski and W. Kołos, in *Molecular Interactions*, Vol. 3, edited by H. Ratajczak and W. J. Orville-Thomas (Wiley, New York, 1982), pp. 1–46.
- [35] M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions: With Formulas, Graphs and Mathematical Tables* (Dover, New York, 1965).
- [36] C. A. Coulson, *Proc. Roy. Soc. Edinb. A-MA* **61**, 20 (1941).
- [37] J. D. Morgan, III and B. Simon, *Int. J. Quant. Chem.* **17**, 1143 (1980).
- [38] D. Levin, *Int. J. Comput. Math.* **3**, 371 (1972).
- [39] W. H. Press, S. A. Teukolsky, W. T. Vetterling, and B. P. Flannery, *Numerical Recipes 3rd Edition: The Art of Scientific Computing* (Cambridge University Press, New York, 2007).
- [40] E. J. Weniger, *Comput. Phys. Rep.* **10**, 189 (1989).
- [41] T. Ćwiok, B. Jeziorski, W. Kołos, R. Moszyński, and K. Szalewicz, *J. Mol. Struct. THEOCHEM* **307**, 135 (1994).
- [42] T. Ćwiok, B. Jeziorski, W. Kołos, R. Moszyński, J. Rychlewski, and K. Szalewicz, *Chem. Phys. Lett.* **195**, 67 (1992).
- [43] B. Jeziorski, K. Szalewicz, and G. Chałasiński, *Int. J. Quant. Chem.* **14**, 271 (1978).
- [44] T. Ćwiok, B. Jeziorski, W. Kołos, R. Moszyński, and K. Szalewicz, *J. Chem. Phys.* **97**, 7555 (1992).
- [45] T. C. Scott, J. F. Babb, A. Dalgarno, and J. D. Morgan, III, *J. Chem. Phys.* **99**, 2841 (1993).
- [46] J. H. Bartlett, *Phys. Rev.* **98**, 1067 (1955).