Determination of the exchange interaction energy from the polarization expansion of the wave function

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The exchange contribution to the energy of the hydrogen atom interacting with a proton is calculated from the polarization expansion of the wave function using the conventional surface-integral formula and two formulas involving volume integrals: the formula of the symmetry-adapted perturbation theory (SAPT) and the variational formula recommended by us. At large internuclear distances R, all three formulas yield the correct expression $-(2/e)Re^{-R}$, but they approximate it with very different convergence rates. In the case of the SAPT formula, the convergence is geometric with the error falling as 3^{-K}, where K is the order of the applied polarization expansion. The error of the surface-integral formula decreases exponentially as $a^K/(K+1)!$, where $a = \ln 2 - \frac{1}{2}$. The variational formula performs best, its error decays as $K^{1/2}[a^K/(K+1)!]^2$. These convergence rates are much faster than those resulting from approximating the wave function through the multipole expansion. This shows the efficiency of the partial resummation of the multipole series effected by the polarization expansion. Our results demonstrate also the benefits of incorporating the variational principle into the perturbation theory of molecular interactions.

It is impossible to understand the world without the knowledge of intermolecular interactions [1]. Not only do they govern the properties of gases [2], liquids [3], and solids [4], but also they influence chemical reactivity [5] and determine the structure of complex biological systems [6].

The current understanding of molecular interactions, based on the decomposition of the interaction energy E_{int} into electrostatic, induction, dispersion, and exchange components, is provided by the symmetry-adapted perturbation theory (SAPT) [7,8]. In this theory the molecular interaction is treated by a perturbation procedure in which the proper symmetry of the wave function is forced in each order [9,10] and the noninteracting monomers are used at the zeroth-order approximation. In contrast to the more conventional supermolecular approach, in which E_{int} is calculated as (a small) difference of large absolute energies, the perturbation treatment of molecular interactions is free from basis-set superposition error (BSSE) [11], does not rely on fortuitous error cancellation of large numbers, and provides a clear connection between monomer properties and the interaction energy components. For further discussion of the merits and applications of SAPT we refer the reader to recent reviews [12,13].

The most straightforward perturbation treatment of molecular interactions, known as the *polarization approximation* [14] or *polarization expansion*, consists of an application of the standard Rayleigh-Schrödinger perturbation theory, with the zeroth-order Hamiltonian H_0 taken as the sum of the noninteracting monomer Hamiltonians, and the perturbation V (the interaction operator) defined as $V = H - H_0$, where H is the electronic Hamiltonian of the system. Polarization expansion provides the correct, valid for all intermolecular distances R, definitions of the electrostatic, induction, and

dispersion contributions to the interaction energy [7]. It is well known, however, that in a practically computable finite order, the polarization expansion for the energy is not able to recover the exchange energy, the basic repulsive component of the interaction potential that determines the structure of molecular complexes and solids. It is also known [15,16] that the polarization series provides the asymptotic expansion of the *primitive function* Φ [14],

$$\Phi = \varphi^{(0)} + \varphi^{(1)} + \cdots + \varphi^{(K)} + O(R^{-\kappa(K+1)}), \quad (1)$$

where $\varphi^{(k)}$ is the kth-order (in V) polarization correction to the wave function and $\kappa = 3$ for interactions of neutral monomers, and $\kappa = 2$ when at least one of the monomers is charged. Equation (1) represents the *genuine* primitive function in the sense of Kutzelnigg [17], i.e., the function which, after appropriate symmetry projections $\mathcal{A}_\nu$, yields correctly all asymptotically degenerate wave functions Ψ_ν of the interacting system, $\mathcal{A}_\nu \Phi = \Psi_\nu$, and which is localized in the same way as the zeroth-order wave function $\varphi^{(0)}$. Using the exact wave functions Ψ_ν, Eq. (1) can be written in an equivalent, mathematically more precise form [16]

$$\|\Psi_\nu - \mathcal{A}_\nu \Phi^{(K)}\| = O(R^{-\kappa(K+1)}), \quad (2)$$

where $\Phi^{(K)} = \varphi^{(0)} + \varphi^{(1)} + \cdots + \varphi^{(K)}$ is the polarization function through the Kth order and $\|\cdot\|$ is the usual $\mathcal{L}^2$ norm.

While methods of calculating the large-R asymptotic behavior of the polarization energies (electrostatics, induction, dispersion) are well developed and there is a great deal of information about the corresponding asymptotic constants [7], very little is known about the asymptotic behavior of exchange energy. Even the functional form of its asymptotic decay for system as simple as two hydrogen atoms still stirs controversy [18–20]. The reason for the difficulty is that the exchange energy, as the result of the resonance tunneling of the electrons between the Coulomb wells of the interacting atoms, is sensitive to the wave-function values in the classically forbidden region of multidimensional configuration space. The

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conventional, basis-set-based methods of electronic structure theory are not well suited to accurately represent the wave function in this region.

Only for the interaction of the hydrogen atom with a proton, i.e., for the H_2^+ system, the asymptotic expansion of the exchange energy is known from the tour de force study of Refs. [21,22]. For this system the exchange energy $J(R)$ is defined as

$$J(R) = \tfrac{1}{2}(E_g - E_u), \tag{3}$$

where E_g and E_u are the energies of the lowest *gerade* and *ungerade* states of the Hamiltonian $H = -\Delta/2 - r_a^{-1} - r_b^{-1} + R^{-1}$, r_a and r_b being the distances of the electron to the nuclei a and b. Using semiclassical methods the authors of Refs. [21,22] found that for H_2^+ the exchange energy has the following asymptotic expansion:

$$J(R) \sim (2/e)\, R\, e^{-R}(j_0 + j_1\, R^{-1} + j_2\, R^{-2} + \cdots), \tag{4}$$

where $j_0 = -1$, $j_1 = -1/2$, etc. Atomic units $\hbar = m_e = e = 1$ are used in Eq. (4) and throughout the paper.

In this work we shall consider three formulas expressing $J(R)$ in terms of Φ. The physical picture of electrons tunneling from one potential well to the other is reflected by the surface-integral formula [23–25]. Using the notation appropriate for H_2^+ this formula takes the form

$$J_{\mathrm{surf}}[\Phi] = \frac{\int_M \Phi \boldsymbol{\nabla} \Phi\, d\mathbf{S}}{\langle \Phi | \Phi \rangle - 2 \int_{\mathrm{right}} \Phi^2\, dV}, \tag{5}$$

where M is the plane perpendicular to the bond axis passing through the center of the molecule and the volume integral with subscript "right" is taken over that half of the space restricted by M where the function Φ is not localized. Surface integrals, which are cumbersome in the case of many-electron systems, can be avoided if one uses volume-integral formulas: the so-called SAPT formula [26], and the variational formula recommended recently by the present authors [27]. In the notation specified for H_2^+ these formulas have the form

$$J_{\mathrm{SAPT}}[\Phi] = \frac{\langle \varphi^{(0)}|V\mathcal{P}\Phi\rangle\langle\varphi^{(0)}|\Phi\rangle - \langle\varphi^{(0)}|V\Phi\rangle\langle\varphi^{(0)}|\mathcal{P}\Phi\rangle}{\langle\varphi^{(0)}|\Phi\rangle^2 - \langle\varphi^{(0)}|\mathcal{P}\Phi\rangle^2},$$
$$\tag{6}$$

$$J_{\mathrm{var}}[\Phi] = \frac{\langle \Phi|H\mathcal{P}\Phi\rangle\langle\Phi|\Phi\rangle - \langle\Phi|H\Phi\rangle\langle\Phi|\mathcal{P}\Phi\rangle}{\langle\Phi|\Phi\rangle^2 - \langle\Phi|\mathcal{P}\Phi\rangle^2}, \tag{7}$$

where $\mathcal{P}$ is the operator inverting the electron coordinates with respect to the center of the molecule. Equation (6) is obtained in the so-called symmetrized Rayleigh-Schrödinger (SRS) perturbation theory [10,28,29] specified for H_2^+ or H_2. Because of its simplicity the SRS theory is the only variant of SAPT that is routinely applied to large many-electron systems [12,13].

A direct calculation of the primitive function Φ without a prior knowledge of Ψ_v is very difficult. In principle Φ can be obtained using the Hirschfelder-Silbey (HS) perturbation expansion [30], which quickly converges for H_2^+ [31] and leads to very accurate values of the exchange energy when formulas (5) and (6) are evaluated with the converged Φ [26]. However,

the HS theory is not feasible for many-electron systems and we have at our disposal only asymptotic approximations to Φ, given by the multipole series for the wave function [7,15] or by the polarization expansion of Eq. (1). The analytic study for H_2^+ has shown [32] that the multipole expansion of Φ, when inserted in Eqs. (5)–(7), predicts correctly the leading j_0 term in Eq. (4) but the convergence to the exact result is slow (harmonic) when the SAPT formula is used and geometric with the ratio of 1/2 and 1/4 when the surface-integral and variational formulas are used, respectively.

In the present work we show the results that one obtains using the polarization expansion for Φ, i.e., the results of evaluating Eqs. (5)–(7) with the function $\Phi^{(K)}$. Since the perturbation V has the infinite multipole expansion, each polarization correction $\varphi^{(n)}$ accounts for the interaction of infinitely many multipoles. The polarization expansion not only includes the charge-overlap effects [7] but also may be viewed as a selective, infinite-order resummation of the multipole expansion. One can expect, then, that the polarization expansion of the wave function can give better approximation to the exchange energy than the multipole expansion.

I. WAVE-FUNCTION ASYMPTOTICS

The polarization corrections to the wave function, referred to for brevity as *polarization functions*, are defined by the recurrence relations

$$(H_0 - E_0)\varphi^{(k)} = -V\varphi^{(k-1)} + \sum_{m=1}^{k} E^{(m)}\varphi^{(k-m)}, \tag{8}$$

where $E^{(k)} = \langle\varphi^{(0)}|V\varphi^{(k-1)}\rangle$ and the ground state of the hydrogen atom a is taken as the zeroth-order approximation, i.e., $\varphi^{(0)} = \pi^{-1/2}e^{-r_a}$, $E_0 = -1/2$.

In our previous work [27], we showed that the asymptotics of $J(R)$, i.e., the value j_0 of Eq. (4), when calculated from Eqs. (5)–(7) depends only on the values of Φ on the line joining the nuclei. Thus, if the polarization function $\varphi^{(k)}$ is written as $\varphi^{(0)} f^{(k)}(r_a, \theta_a)$, where θ_a is the angle at nucleus a in the triangle formed by the nuclei and the electron, then the angular dependence of $f^{(k)}(r_a, \theta_a)$ does not affect the value of j_0 and the function $f^{(k)}(r_a, \theta_a)$ can be replaced by its value at $\theta_a = 0$, i.e., by $f^{(k)}(r_a, 0)$. We have shown [32] that in the large-R asymptotic expansion of $f^{(k)}(r_a, 0)$,

$$f^{(k)}(r_a, 0) \sim \sum_n R^{-n} \sum_{m=0}^{n} t_{nm}^{(k)} r_a^m, \tag{9}$$

only the dominant $m = n$ terms contribute to the asymptotics of $J(R)$. Thus, in calculating this asymptotics, $f^{(k)}(r_a, 0)$ can be replaced by the simpler function

$$\widetilde{f}^{(k)}(r_a) \sim \sum_n t_{nn}^{(k)}(r_a/R)^n. \tag{10}$$

In Ref. [32] we have shown that the coefficients $t_n^{(k)} \equiv t_{nn}^{(k)}$ in Eq. (10) satisfy the recurrence relation

$$t_n^{(k)} = \frac{1}{n}\sum_{j=2k-2}^{n-2} t_j^{(k-1)}, \tag{11}$$

with the initial $k = 0$ values given by $t_n^{(0)} = \delta_{n0}$ (we assume that a sum is zero when the lower summation limit exceeds the upper one). Although the closed-form expression for $t_n^{(k)}$ is unknown, we shall show that the series of Eq. (10) converges for $r_a < R$ (hence on the line joining the nuclei) to the expression

$$\widetilde{f}^{(k)}(r_a) = [-r_a/R - \ln(1 - r_a/R)]^k/k!. \qquad (12)$$

Equation (12) means that $g^{(k)}(z) = [-z - \ln(1 - z)]^k/k!$ is the generating function of $t_n^{(k)}$. To prove this it is sufficient to note that $g^{(k)}(z)$ satisfies the equation

$$\frac{d}{dz} g^{(k)}(z) = \frac{z}{1 - z} g^{(k-1)}(z), \qquad (13)$$

expand both sides of Eq. (13) in powers of z, and compare coefficients at z^n. One may note that the functions $\widetilde{f}^{(k)}(r_a)$ form an exponential series, which is consistent with the analysis of Ref. [33]. The series of functions $\widetilde{f}^{(k)}(r_a)$ converges to $e^{-r_a/R}/(1 - r_a/R)$, the function obtained earlier via the WKB method [24,25] and shown to represent the dominant contribution to the infinite-order polarization function [34]. Thus, our results agree with the findings of Ref. [34].

II. SURFACE-INTEGRAL FORMULA

We shall denote by $j_0^{\text{surf}}[\Phi^{(K)}]$, $j_0^{\text{SAPT}}[\Phi^{(K)}]$, and $j_0^{\text{var}}[\Phi^{(K)}]$ the approximations to j_0 obtained when the polarization function $\Phi^{(K)}$ is used in the surface-integral, SAPT, and variational formulas, Eqs. (5)–(7), respectively. Tang *et al.* [35] showed that the asymptotics of $J_{\text{surf}}[\Phi]$ can be determined from the expression $-R e^{-R}[F(R/2,0)]^2/2$, where the function $F(r_a,\theta_a)$ is defined by the factorization $\Phi = \varphi^{(0)} F(r_a,\theta_a)$. Approximating $F(r_a,0)$ by the asymptotics of its Kth-order polarization expansion we find

$$j_0^{\text{surf}}[\Phi^{(K)}] = -\frac{e}{4}\left[\sum_{k=0}^{K} \widetilde{f}^{(k)}\left(\frac{R}{2}\right)\right]^2 = -\frac{e}{4}\left(\sum_{k=0}^{K} \frac{a^k}{k!}\right)^2, \qquad (14)$$

where

$$a = \ln 2 - \frac{1}{2} \approx 0.19. \qquad (15)$$

Equation (14) has been obtained in Ref. [35] using a different derivation. The correct value of j_0 is recovered by the $K \to \infty$ limit of $j_0^{\text{surf}}[\Phi^{(K)}]$ equal to $-e^{2a+1}/4 = -1$. Furthermore, the error of $j_0^{\text{surf}}[\Phi^{(K)}]$ decreases rapidly, as

$$j_0 - j_0^{\text{surf}}[\Phi^{(K)}] = -\sqrt{e}\,\frac{a^{K+1}}{(K+1)!} + O\left(\frac{a^{K+2}}{(K+2)!}\right), \qquad (16)$$

in the same way as the truncation error of the exponential series. Figure 1 shows the accuracy of Eq. (16).

III. VARIATIONAL FORMULA

Since $\langle\Phi^{(K)}|\Phi^{(K)}\rangle = 1 + O(R^{-4})$ and $\langle\Phi^{(K)}|H\Phi^{(K)}\rangle = E_0 + O(R^{-4})$, the coefficient $j_0^{\text{var}}[\Phi^{(K)}]$ can be extracted from the expression

$$J_{\text{var}}^*[\Phi^{(K)}] = \langle\Phi^{(K)}|(H - E_0)\mathcal{P}\Phi^{(K)}\rangle. \qquad (17)$$
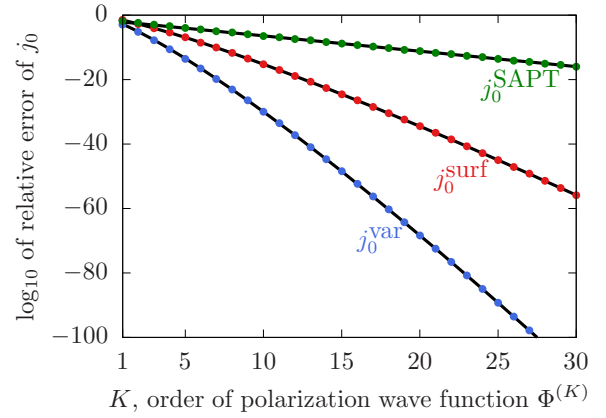

FIG. 1. Logarithms of errors of j_0 calculated using the variational, SAPT, and surface-integral formulas. Dots are the calculated values; solid lines, the error estimates of Eqs. (16), (38), and (43).

Writing $\Phi^{(K)} = \varphi^{(0)} F^{(K)}$ one can show that $j_0^{\text{var}}[\Phi^{(K)}]$ can be obtained from an even simpler formula:

$$J_{\text{var}}^{**}[\Phi^{(K)}] = \left\langle \mathcal{P}\varphi^{(0)} F^{(K)} \middle| \varphi^{(0)}\left(\frac{\partial}{\partial r_a} F^{(K)} + V F^{(K)}\right)\right\rangle, \qquad (18)$$

in which the Laplacian of $F^{(K)}$ was neglected since it does not contribute to $j_0^{\text{var}}[\Phi^{(K)}]$.

Approximating $F^{(K)}$ by $\widetilde{F}^{(K)} = \widetilde{f}^{(0)} + \widetilde{f}^{(1)} + \cdots + \widetilde{f}^{(K)}$ and noting that $\partial\widetilde{F}^{(k)}/\partial r_a + V\widetilde{F}^{(k)} = \widetilde{f}^{(k)}$, cf. Eq. (13), one can represent the asymptotics of $J_{\text{var}}^{**}[\Phi^{(K)}]$ in terms of integrals

$$\langle\mathcal{P}\varphi^{(0)} \widetilde{f}^{(k_1)}|V\varphi^{(0)} \widetilde{f}^{(k_2)}\rangle = -\frac{R\, e^{-R}}{4 k_1!\, k_2!} L(k_1,k_2)\left[1 + O\left(\frac{1}{R}\right)\right], \qquad (19)$$

where

$$L(k_1,k_2) = \int_{-1}^{1} d\eta\, (1 + \eta)^2 [\gamma(\eta)]^{k_1} [\gamma(-\eta)]^{k_2}, \qquad (20)$$

and $\gamma(\eta) = (\eta - 1)/2 + \ln 2 - \ln(\eta + 1)$. Equations (19) and (20) follow from the integration in the elliptic coordinates, $\xi = (r_a + r_b)/R, \eta = (r_a - r_b)/R$, and the integration by parts procedure of Eq. (29) in Ref. [27].

Using Eqs. (18) and (19) one obtains

$$\frac{2}{e} j_0^{\text{var}}[\Phi^{(K)}] = -\frac{1}{4K!} \sum_{k=0}^{K} \frac{L(k,K)}{k!}. \qquad (21)$$

For $K = 1$ one finds

$$\frac{2}{e} j_0^{\text{var}}[\Phi^{(1)}] = -\frac{1}{4}\big[L(0,1) + L(1,1)\big] = -\frac{989}{540} + \frac{\pi^2}{9}, \qquad (22)$$

in agreement with Ref. [36]. For arbitrary K Eq. (21) can be rewritten as

$$\frac{2}{e} j_0^{\text{var}}[\Phi^{(K)}] = -\frac{1}{4K!}\left[M(K) - \sum_{p=1}^{\infty} T_p^K\right], \qquad (23)$$

where

$$T_p^K = L(K + p, K)/(K + p)!, \qquad (24)$$

and

$$M(K) = \sum_{k=0}^{\infty} \frac{L(k,K)}{k!}. \qquad (25)$$

Changing the order of summation and integration, collapsing the exponential series, and using the variable change $x = \gamma(-\eta)$ we obtain

$$M(K) = \frac{8}{e} \int_0^{\infty} x^K e^{-x} \, dx = \frac{8K!}{e}. \qquad (26)$$

Since the second term in the square brackets on the right-hand side of Eq. (23) vanishes when $K \to \infty$, cf. Eqs. (37) and (28), we see that $j_0^{\text{var}}[\Phi^{(K)}]$ converges to the correct value $j_0 = -1$.

IV. VARIATIONAL FORMULA—THE CONVERGENCE RATE

We shall show that the residual series in Eq. (23) can be estimated (at large K) by its first term, T_1^K. For large K and $p = 1,2$ the integrals $L(K + p, K)$ of Eq. (24) can be approximated using the Laplace method [37]. To this end we rewrite them as

$$L(K + p, K) = \int_{-1}^{1} (1 + \eta)^2 [\gamma(\eta)]^p e^{K\lambda(\eta)} \, d\eta, \qquad (27)$$

where $\lambda(\eta) = \ln [\gamma(\eta)\gamma(-\eta)]$. As $\lambda(\eta)$ has a single maximum at $\eta = 0$, for large K only $\eta \in [-\epsilon, \epsilon]$ with a small ϵ contribute significantly to Eq. (27). Approximating $\lambda(\eta)$ for $|\eta| < \epsilon$ by the Taylor expansion, $\lambda(\eta) = \lambda_0 + \lambda_2 \eta^2 + O(\eta^3)$ converts Eq. (27) into the Gaussian integral (see Ref. [37] for details),

$$L(K + p, K) = \sqrt{\pi/(K|\lambda_2|)} \, a^{2K+p} [1 + O(K^{-1})], \qquad (28)$$

where $\lambda_2 = (4a - 1)/(4a^2)$. We use Eq. (28) to estimate $p = 1$ and $p = 2$ terms in the residual series in Eq. (23). Equation (28) is not valid for large p so to estimate the $p > 2$ terms we use the Schwartz inequality

$$L(K + p, K) \leqslant (P_{2p} Q_{2K})^{1/2}, \qquad (29)$$

where

$$Q_m = \int_{-1}^{1} e^{m\lambda(\eta)} d\eta, \qquad (30)$$

and

$$P_m = \int_{-1}^{1} (1 + \eta)^4 [\gamma(\eta)]^m d\eta. \qquad (31)$$

Using the Laplace method once more we have

$$Q_m = \sqrt{\pi/(m|\lambda_2|)} \, a^{2m} \left[1 + O\left(\frac{1}{m}\right)\right]. \qquad (32)$$

The variable change $t = \ln 2 - \ln(\eta + 1)$ shows that

$$P_m = 32 \int_0^{\infty} e^{-5t} [e^{-t} + t - 1]^m dt. \qquad (33)$$

Since $e^{-t} + t - 1 \leqslant t$ for $t \geqslant 0$, it follows that $P(m) \leqslant (32/5)m!/5^m$, so that $T_p^K \leqslant \widetilde{T}_p^K$, where

$$\widetilde{T}_p^K = 4\left[\tfrac{2}{5}(2p)! Q_{2K}\right]^{1/2} 5^{-p}/(K + p)!. \qquad (34)$$

It can be shown that $\widetilde{T}_{p+1}^K/\widetilde{T}_p^K \leqslant 2/5$, so that the infinite sum of $\widetilde{T}_p^K$, and consequently T_p^K, can be bounded by the geometric series with the ratio equal to $2/5$,

$$\sum_{p=3}^{\infty} T_p^K \leqslant \sum_{p=3}^{\infty} \widetilde{T}_p^K \leqslant \sum_{p=3}^{\infty} \widetilde{T}_3^K \left(\frac{2}{5}\right)^{p-3} = \frac{5}{3} \widetilde{T}_3^K. \qquad (35)$$

Using Eqs. (35), (34), and (28), we find that

$$\frac{1}{T_1^K} \sum_{p=3}^{\infty} T_p^K \leqslant \frac{D \, K^{1/4}}{(K + 2)(K + 3)} [1 + O(K^{-1})], \qquad (36)$$

where $D = 16[(1 - 4a)/(2\pi)]^{1/4}/(25a^{3/2})$. Therefore, the $p \geqslant 3$ contributions to the series on the right-hand side of Eq. (23) are negligible in comparison with the $p = 1$ term. In view of Eq. (28), $T_2^K \sim a^{2K+2}/(K + 2)!$, hence the term with $p = 2$ on the right-hand side of Eq. (23) is also negligible when compared to the $p = 1$ term. Finally

$$\sum_{p=1}^{\infty} T_p^K = T_1^K [1 + O(K^{-1})]. \qquad (37)$$

Thus, the error of $j_0^{\text{var}}[\Phi^{(K)}]$ is dominated by the $p = 1$ term in the sum in Eq. (23),

$$j_0 - j_0^{\text{var}}[\Phi^{(K)}] = -\frac{A \, a^{2K+2}}{\sqrt{K} K!(K + 1)!} [1 + O(K^{-1})], \qquad (38)$$

where $A = e\sqrt{\pi}/(4\sqrt{1 - 4a})$. The rapid fall-off of the error of $j_0^{\text{var}}[\Phi^{(K)}]$ can be seen in Fig. 1.

V. SAPT FORMULA

To obtain $j_0^{\text{SAPT}}[\Phi^{(K)}]$ it is sufficient to consider the following approximation to $J_{\text{SAPT}}[\Phi^{(K)}]$:

$$J_{\text{SAPT}}^*[\Phi^{(K)}] = \langle \varphi^{(0)} | V \mathcal{P} \varphi^{(0)} F^{(K)} \rangle. \qquad (39)$$

Approximating $F^{(K)}$ by the sum of functions $\widetilde{f}^{(k)}(r_a)$ one can represent $j_0^{\text{var}}[\Phi^{(K)}]$ in terms of integrals $\langle \varphi^{(0)} | V \mathcal{P} \varphi^{(0)} \widetilde{f}^{(k)}(r_a) \rangle$. Using Eq. (19) one obtains

$$\frac{2}{e} j_0^{\text{SAPT}}[\Phi^{(K)}] = -\frac{1}{4} \sum_{k=0}^{K} \frac{L(k)}{k!}, \qquad (40)$$

with $L(k) = L(k,0)$. When $K \to \infty$, the sum on the right-hand side is equal to $M(0)$, so in view of Eq. (25), $j_0^{\text{SAPT}}[\Phi^{(K)}]$ converges to the correct value $j_0 = -1$.

To calculate the error of $j_0^{\text{SAPT}}[\Phi^{(K)}]$ we need the integrals

$$L(k) = 8 \int_0^{\infty} e^{-3t} [e^{-t} + t - 1]^k dt \qquad (41)$$

obtained from Eq. (20) using the variable change $t = \ln 2 - \ln(\eta + 1)$. Repeated application of the binomial theorem yields

$$L(k) = \sum_{l=0}^{k} \frac{8k! e_{k-l}(-l - 3)}{l!(l + 3)^{k-l+1}}, \qquad (42)$$

where $e_n(x)$ is the exponential sum function, i.e., the series of e^x truncated after the $x^n/n!$ term. The large-k asymptotics of

$L(k)$ is given by the first $l = 0$ term in the sum in Eq. (42). It follows that

$$j_0 - j_0^{\text{SAPT}}[\Phi^{(K)}] = -\frac{1}{6e^2} 3^{-K} + O(4^{-K}). \quad (43)$$

The error of $j_0^{\text{SAPT}}[\Phi^{(K)}]$ can be compared to the errors of the other two formulas in Fig. 1.

VI. SUMMARY AND CONCLUSIONS

By solving analytically the model system of the hydrogen atom interacting with a proton we found that all three exchange energy formulas considered by us correctly predict the large-R behavior of the exchange energy if the primitive function is approximated by the standard polarization expansion. The correct limit is, however, approached with very different convergence rates. In the case of the SAPT formula, the convergence is geometric with the error decaying as $1/3^K$, where K is the order of the applied polarization theory. The convergence of the surface-integral formula is exponential, with the error decreasing as $a^K/(K + 1)!$, where $a = \ln 2 - 1/2$. The best convergence occurs for the variational formula, for which the error falls off as $K^{1/2}[a^K/(K + 1)!]^2$. The observed convergence rates are significantly faster than those resulting from approximating the primitive function through the multipole expansion [27,32]. To make a meaningful comparison, cf. Table I, we note that $\Phi^{(K)}$ and the sum of the multipole expansion through the $(2K)$th order in $1/R$, denoted by Φ_{2K}, are both accurate through the $(2K)$th order in $1/R$. However, $\Phi^{(K)}$, unlike Φ_{2K}, includes a selective infinite-order

TABLE I. Decay rate of the error of the leading term of exchange energy calculated using truncated multipole Φ_{2K} (Ref. [32]) and polarization $\Phi^{(K)}$ series. $a = \ln 2 - \frac{1}{2} \approx 1/5$.

	$\Phi = \Phi_{2K}$	$\Phi = \Phi^{(K)}$
$j_0^{\text{surf}}[\Phi]$	$\dfrac{1}{4^K}$	$\dfrac{a^K}{(K+1)!}$
$j_0^{\text{SAPT}}[\Phi]$	$\dfrac{1}{K^2}$	$\dfrac{1}{3^K}$
$j_0^{\text{var}}[\Phi]$	$\dfrac{1}{16^K}$	$\dfrac{a^{2K}}{K!(K+1)!\sqrt{K}}$

summation of higher R^{-k}, $k > 2K$ terms. The inspection of Table I shows that this infinite-order selective summation is very effective in computing the exchange energy, independently of the exchange energy expression employed.

The main conclusion of our investigation is that the exchange energy, an electron tunneling effect, can be determined from the knowledge of the wave function which reflects only the polarization mechanism of interatomic interaction. We have shown that this determination is particularly effective when the variational principle is employed in the perturbation treatment of molecular interactions. We expect that this conclusion is general and applies also to interactions of larger systems.

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