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 \( \text{gerade} \) and \( \text{ungerade} \) 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.

I. INTRODUCTION

From the very advent of quantum chemistry, the exchange energy has been one of 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 the half of the difference between the energies of the lowest \( \text{gerade} \) and \( \text{ungerade} \) states:

\[
J = \frac{1}{2}(E_g - E_u).
\]  

(1)

Being the simplest system with a chemical bond, \( H_2^+ \) is a very important model for more complicated systems. It has served as a benchmark system for Symmetry Adapted Perturbation Theories (SAPT), see e.g. [4, 5]. It was also proposed as a model of alkali 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, \(- (2/e) R e^{-R}\), of the asymptotic expansion of \( J \):

\[
J(R) = 2e^{-R-1}R(j_0+j_1 R^{-1}+j_2 R^{-2}+j_3 R^{-3}+\ldots) \]  

(2)

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

\[
J_{surf}[\phi] = \frac{-\int_M \phi \nabla \phi dS}{\langle \phi | \phi \rangle} - \int_{\text{right}} \phi^2 dV,
\]  

(3)

where \( \phi \) is the so-called primitive function [8], which will be defined later, and “right” denotes the half of the whole space right to the median plane (we use atomic units in this equation and throughout the paper). A similar calculation was included in the Landau and Lifschitz’s textbook on quantum mechanics [9]. Bardsley et al. [10] used exponential parametrization of the localized function \( \phi \) 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 \( \phi \) of Herring and Holstein, as was 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 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 first 52 \( j_k \)’s of the expansion (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 second, third and fourth term of (2) with relative errors of \(-2.8\%\), \(-17.8\%\) and \(36.9\%\), respectively. Nevertheless, no previ-

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ous work has succeeded in obtaining the expansion (2) by means of standard \textit{ab initio} approaches of quantum chemistry. As Whitten and Byers-Brown have pointed out [21], this is partly due to the fact that Rayleigh-Schrödinger 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 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 (2) using a volume integral formula of symmetry-adapted perturbation theory (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 Section II we recall the definition of the primitive function $\phi$ and derive the volume integral formula for the exchange energy. Section III presents the approximations to $\phi$ that we use: the Hirschfelder-Silbey and Rayleigh-Schrödinger perturbation theories. We describe the computational aspects of our study (the basis sets, extrapolation and fitting techniques) in Section IV. Section V describes 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, and the accuracy of different approximations of $J$. Our article is closed with concluding remarks in Section VI.

\section{Exchange Energy and the Primitive Function}

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

The primitive function $\phi$ is defined as a linear combination of the asymptotically degenerate \textit{gerade} and \textit{ungerade} wave functions, $\psi_g$ and $\psi_u$,

$$\phi = c_1 \psi_g + c_2 \psi_u,$$

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

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

for all $n > 0$, where $\phi_0 = 1s_a$ is the ground-state wave function of the hydrogen atom centered on the 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 \textit{genuine primitive function} for the function satisfying the condition (5). Since we will use perturbation approximations to the primitive function, it is convenient to impose intermediate normalization:

$$\langle \phi_0 | \phi \rangle = 1.$$

Introducing interaction energies $E_g$ and $E_u$,

$$E_g = E_g - E_0, \quad E_u = E_u - E_0,$$

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

$$\begin{align*}
(H_0 - E_0)\psi_g &= (E_g - V)\psi_g, \\
(H_0 - E_u)\psi_u &= (E_u - V)\psi_u.
\end{align*}$$

The unperturbed Hamiltonian $H_0$ and the interaction operator $V$ are

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

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

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{coor.png}
\caption{Coordinates used in our study. Nuclei are denoted by $a$ and $b$.}
\end{figure}

Fig. 1 shows coordinates that we use. Wave functions $\psi_g$ and $\psi_u$ are expressed through $\phi$ as

$$\psi_g = A_g \phi, \quad \psi_u = A_u \phi,$$

where $A_g$ and $A_u$ are the symmetry projectors defined as

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

After inserting formulas (10) into (8) and taking inner products with $\phi_0$, one obtains

$$\begin{align*}
E_g \langle \phi_0 | (1 + P_{ab}) \phi \rangle &= \langle \phi_0 | V (1 + P_{ab}) \phi \rangle, \\
E_u \langle \phi_0 | (1 - P_{ab}) \phi \rangle &= \langle \phi_0 | V (1 - P_{ab}) \phi \rangle.
\end{align*}$$

The solution for $J = \frac{1}{2}(E_g - E_u) = \frac{1}{2}(E_g - E_a)$ 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 $\phi$ is expanded in powers of $V$, Eq. (13) generates the expansions of the exchange energy appearing in the symmetry-adapted perturbation theory \[28-30\]. We will 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 $\phi$ could be obtained as a combination of variationally calculated $\psi_g$ and $\psi_u$ in appropriate dimer bases. This would however quickly lead to a loss of accuracy for large $R$. We therefore decided to test other approximations to $\phi$, that can be obtained directly, without the knowledge of $\psi_g$ and $\psi_u$.

The Hirschfelder-Silbey perturbation theory (HS) \[31\] is constructed to provide a perturbation expansion of the primitive function in orders of the perturbation $V$

$$\phi = \phi_{(0)}^{HS} + \phi_{(1)}^{HS} + \phi_{(2)}^{HS} \cdots .$$

It converges to the results of variational calculation with the same basis set, provided that this basis set is invariant under symmetry operations \[32\]. The equations for the consecutive corrections $\phi_{(n)}^{HS}$ to the HS wave function are \[32\]:

$$\phi_{(n)}^{HS} = -R_0 V \phi_{(n-1)}^{HS} + \sum_{k=1}^{n} E_{(k)}^{g} R_0 A_g \phi_{(1)}^{HS}$$

$$+ \sum_{k=1}^{n} E_{(k)}^{u} R_0 A_u \phi_{(n-k)}^{HS} ,$$

where the energy corrections $E_{(k)}^{g}$ and $E_{(k)}^{u}$ are given by

$$E_{(k)}^{(n)} = \langle \phi_0 | A_{(k)} \phi_0 \rangle^{-1} \left( \langle \phi_0 | V A_{(k)} \phi_{(n-1)}^{HS} \rangle $$

$$- \sum_{k=1}^{n-1} E_{(k)}^{(n)} \langle \phi_0 | A_i \phi_{(n-k)}^{HS} \rangle \right) , \quad \nu = g, u .$$

The zero-order wave function and energy are those of the unperturbed hydrogen atom, $\phi_{(0)}^{HS} = \phi_0 \equiv 1 s_a$, $E_{(0)}^{g} = E_{(0)}^{u} = E_0 \equiv -1/2$. The resolvent $R_0$ is defined by

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

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

The standard Rayleigh-Schrödinger 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 \[34\]:

$$\psi_{(n)} = A_{(n)} \sum_{k=0}^{n} \phi_{RS}^{(k)} + O(R^{-k(n+1)}), \quad \nu = g, u ,$$

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

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

and the energy corrections $E_{RS}^{(n)}$ are calculated as

$$E_{RS}^{(n)} = \langle \phi_0 | V \phi_{RS}^{(n-1)} \rangle .$$

The unperturbed wave function, unperturbed energy and reduced resolvent are the same as in the HS theory.

IV. COMPUTATIONAL ASPECTS

Basis set used by us consists of functions

$$\chi_c^{N,M} = N_{N,M} e^{-r_c L^2_{N} (2r_c) r_c P_{M} (\cos \theta_c) ,}$$

where $c = a, b$ and $L^2_{N}(x)$ and $P_{M}(x)$ are the generalized Laguerre and Legendre polynomials, respectively, defined as in e.g. Ref. \[35\]. The angles $\theta_a$ and $\theta_b$ are the interior ones of the triangle given by $r_a$, $r_b$, $R$ (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 $\theta_b$ 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, $\phi_0 = \chi_{a,0}^{0,1}$.

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

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

This reduces linear dependencies in the basis set at large $R$, allowing for accurate calculations of the asymptotic constants $j_k$. Sets of exponents \{(N,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 $\Omega$ constraining $N$ and $M$:

$$N + M \leq \Omega .$$

This hierarchy is useful for making extrapolations to the complete basis set limit. It is advantageous to treat $N$
and $M$ symmetrically in eq. (22). This choice is consistent with the multipole expansion of the wave function, and provides the best convergence at large $R$.

The basis set (20) is appropriate for large internuclear distances $R$ but is inadequate for small ones because of strong linear dependencies appearing at larger values of $\Omega$. 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 $\Omega = 20$ (462 basis functions).

Chipman and Hirschfelder used basis similar to (20), but with monomials in $r_n$ and $r_3$ instead of Laguerre polynomials, when they applied different perturbation theories to $H_2^+$ [4]. The basis (20) restricted to functions centered on the nucleus $\alpha$ 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 $\Omega$-dependence of the computed values of $J$ permits an efficient application of extrapolation technique to accelerate basis set convergence. We used Levin’s $u$-transformation of the form [38]:

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

where $U_n$ is the resulting accelerated sequence, and $Z_i = A_0 + A_1 + \ldots + A_i$ 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 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 6-term Levin $u$-transformation applied to the 6 best basis sets. With this choice we have $Z_n = J(\Omega = n + 15)$, $A_0 = J(\Omega = 15)$, and $A_n = J(\Omega = n + 15) - J(\Omega = n + 14)$ 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):

$$f(R) = \sum_{i=0}^{L} \frac{j_i}{R^i}.$$  \hspace{1cm} (24)

It is important to choose the appropriate degree of the fitting polynomial $L$. A fit with to 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 $R = 60, 62, \ldots, 150$ in the fitting procedure. We used an additional “test set” of 9 internuclear distances $R = 65, 75, \ldots, 145$ to assess the quality of fits. Analysis of the errors given by fits with different $L$ for the 9 points in the test set allowed us to determine the optimal values of $L$. We found that the optimal value of $L$ is 8 when the volume integral formula is used. For the surface integral expression the optimal choice of $L$ is 4.

V. RESULTS AND DISCUSSION

A. Convergence of perturbation theory

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

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

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

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

where $\phi$ stands either for $\phi_{HS}$ or $\phi_{RS}$.

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

In comparison to the HS theory, the convergence properties of the Rayleigh-Schrödinger perturbation expansion are much more complicated [41]. This is reflected in the convergence of the exchange energy corrections $J_{\text{SAPT}}^{(n)}[\phi_{RS}]$ calculated from Eq. (26). These corrections are identical with those of the Symmetrized Rayleigh-Schrödinger perturbation theory (SRS) [42]. For perturbation orders $n$ larger than 10 and smaller than some crit-
also shows that this good convergence can illustrating the con-
\[ R < 1 \] but only marginally at large \( \phi \). For \( n \) larger than \( n_{\text{crit}} \) these ratios are close to 1. Value of \( n_{\text{crit}} \) increases with 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 to obtain the exact limit of the series (26) with \( \phi_{\text{RS}} \) through direct summation. The practical limit is obtained when corrections are summed up to \( n_{\text{crit}} \). 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 form Fig. 2 illustrating the convergence of the HS theory.

We calculated the convergence radius \( \rho \) 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 by a pair of branch points of the lowest eigenvalue of the non-hermitian operator \( H_0 + \zeta V \) [41], where \( \zeta \) is a complex scaling parameter. The radius \( \rho \) has the form \( 1 + \gamma \), with \( \gamma \sim e^{-2R} \) (for instance \( \gamma = 1.84 \cdot 10^{-47} \) for \( R = 60 \) and \( \gamma = 1.90 \cdot 10^{-124} \) for \( R = 150 \)). The physical value of the scaling parameter, \( \zeta = 1 \), lies therefore 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 \( n \to \infty \). In view of the symmetry condition \( P_{ab}\phi_{\text{RS}} = \phi_{\text{RS}} \) the volume integral formula (13) exhibits 0/0 singularity at \( n \to \infty \).

Similarly as for \( H_2 \) this singularity is removable [43] and the series of corrections \( j_{\text{SAPT}}^{(n)}[\phi_{\text{RS}}] \) (i.e. the SRS series for the exchange energy) converges but not necessarily to the true exchange energy. In Sec. V C we show that the limit of this series is asymptotically very close to the true \( J(R) \) and has the same asymptotic coefficients \( j_k \), through \( k = 3 \).

B. Basis set convergence

We found that the convergence of results with respect to \( \Omega \) is very regular for a wide range of internuclear distances. When \( \Omega \) 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.

Fig. 4 also shows that this good convergence can be further improved by the application of the Levin u-
transformation. It can be estimated that values computed as the transformation of six energies \( J(\Omega = 15), \ldots, J(\Omega = 20) \) are of accuracy similar to that possible to calculate with basis \( \Omega = 23 \) (bases \( \Omega = 20 \) and \( \Omega = 23 \) contain 462 and 600 basis functions, respectively).

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

In Fig. 5 we show errors of the asymptotic expansion parameters \( j_k \) for the two considered approximations to the primitive function \( \phi \). These parameters are also given in Table I.

It can be seen that the volume integral formula with \( \phi_{\text{HS}} \) is able to reproduce all \( j_k \) of eq. (2), provided 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 square fitting that the relative error of the SRS exchange energy with respect to the HS one is well represented by a polynomial in \( 1/R \):

\[
\frac{J_{\text{SAPT}}(\phi_{\text{RS}})}{J_{\text{SAPT}}(\phi_{\text{HS}})} - 1 = \frac{w_4}{R^4} + \frac{w_5}{R^5} + \frac{w_6}{R^6} + \frac{w_7}{R^7} + \ldots \tag{27}
\]

with \( w_4 = 8.375 \, 000 \, 000 \, 000 \, (3) \), \( w_5 = 8.375 \, 000 \, 000 \, 000 \, (3) \), \( w_6 = 43.250 \, 000 \, (1) \), \( w_7 = 458.031 \, 3 \, (3) \) (the numbers in parentheses give the uncertainties of the respective last reported digits).

Somewhat surprisingly we found that \( \phi_{\text{HS}} \) and \( \phi_{\text{RS}} \) give practically identical results (up to more than 20 digits) when used in the surface integral formula (3). For instance when \( R = 100 \) and \( \Omega = 20 \) we obtained \( J_{\text{surf}}(\phi_{\text{HS}}) = J_{\text{surf}}(\phi_{\text{RS}}) = -2.749 \, 901 \, 18 \cdot 10^{-42} \) while the exact value is \( J_{\text{exact}} = -2.749 \, 901 \, 24 \cdot 10^{-42} \). 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 \( J_{\text{SAPT}}(\phi_{\text{HS}}) \), defined as \( \Delta J = (J - J_{\text{exact}})/J_{\text{exact}} \), are of the order of \( 10^{-14} \) while the relative errors of \( J_{\text{surf}}(\phi_{\text{HS}}) = J_{\text{surf}}(\phi_{\text{RS}}) \) range from \( 10^{-9} \) to \( 10^{-7} \) for \( R \) between 70 and 150 (the values of \( J_{\text{exact}} \) are calculated from the exact asymptotic constants [17]). The errors of \( J_{\text{SAPT}}(\phi_{\text{RS}}) \) are of the order of \( 10^{-6} \cdot 10^{-8} \) in this range of distances. These increased errors (compared to those of \( J_{\text{SAPT}}(\phi_{\text{HS}}) \)) are not related to a remaining basis set incompleteness but are apparently caused by the incorrect values of the higher \( j_k \) coefficients predicted by \( J_{\text{SAPT}}(\phi_{\text{RS}}) \).

The higher errors resulting from using the surface integral formula can be understood when the quality of the wave function is considered. Accuracy of \( J_{\text{surf}}(\phi) \) depends mainly on the accuracy of the wave function \( \phi \) in the vicinity of the median plane \( M \). We can inspect the quality of any approximate wave function \( \psi \) by analyzing
TABLE I. Values of $j_k$ obtained from different approximations and the exact values calculated by Čížek et al. \cite{cite}. The degrees of the fitting polynomials were 8 for $J_{SAPT}$ and 4 for $J_{surf}$. The values extrapolated from the best six basis sets ($\Omega=15,\ldots,20$) were used in the fits.

| $j_k$ | $J_{exact} \phi_{HS}$ | $J_{SAPT} \phi_{RS}$ | $J_{SAPT} \phi_{RS}$ | $J_{surf} \phi_{RS}$ |
|------|------------------|------------------|------------------|------------------|
| 0    | -1               | -0.999 999 999 999 894 | -0.999 999 999 999 938 | -0.999 999 977 |
| 1    | -0.5             | -0.500 000 000 088  | -0.500 000 000 050  | -0.500 007 1 |
| 2    | 3.125            | 3.125 000 032  | 3.125 000 018  | 3.125 94  |
| 3    | 2.729 166 7     | 2.729 159 8  | 2.729 162 8  | 2.66  |
| 4    | 10.216 1        | 10.217 1   | 1.8           | 12.8   |
| 5    | 37.86           | 37.78      | 25.       | -      |
| 6    | 113.26          | 117.99    | 95.       | -      |
| 7    | 789.2           | 621.0     | 264.     | -      |

the local energy associated with this wave function

$$E_{loc}(r) = \frac{H\psi(r)}{\psi(r)}$$  \hspace{1cm} (28)

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. \cite{cite}.

![Graph](image)

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

Fig. 6 visualizes the errors of $E_{loc}$ for the line joining the nuclei. The reference energy was calculated as the sum of $E_{ip}^{(n)}(HS)$ up to $n = 150$. This graph presents $E_{loc}$ for the symmetrized $\phi_{HS}$ function, $\psi = (1 + P_{ab})\phi_{HS}$, obtained with the $\Omega = 20$ basis set. The graph for $\phi_{RS}$ is not given, as it would be indistinguishable from the one for $\phi_{HS}$ with this scale. It can be seen that the 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 a the median plane, i.e. in the region relevant for the accuracy of the surface integral formula.

VI. CONCLUSIONS

The SAPT volume integral formula and the surface integral formula give very accurate values of the exchange splitting energy when the primitive function is approximated either by the Hirschfelder-Silbey or the Rayleigh-Schrödinger perturbation theories. However, the volume integral expression exhibits much superior basis set convergence than the surface integral one. This is due to the fact that the accuracy of the latter depends strongly on the quality of the wave function (and thus the basis set) at the median plane $M$, i.e. far from the nuclei. The very good (and very similar) basis set convergence of $J_{SAPT} \phi_{RS}$ and $J_{SAPT} \phi_{RS}$ is further improved by extrapolation techniques such as the Levin $u$-transformation. We also found that the values the asymptotic constants obtained from $J_{surf} \phi_{HS}$ and $J_{surf} \phi_{RS}$ are almost identical.

We find it remarkable that the perturbation expansion of $J_{SAPT} \phi_{RS}$, which is equivalent to the Symmetrized Rayleigh-Schrödinger perturbation theory (SRS), does converge but gives accurately only the first four terms of the asymptotic expansion of Eq. (2). The unphysical values of further terms are apparently due to the removable $0/0$ singularity of $J_{SAPT} \phi_{RS}$ in the limit $n \to \infty$.

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 expression can be more easily employed in case of many-electron systems, both ionic and neutral, than the surface integral one.

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