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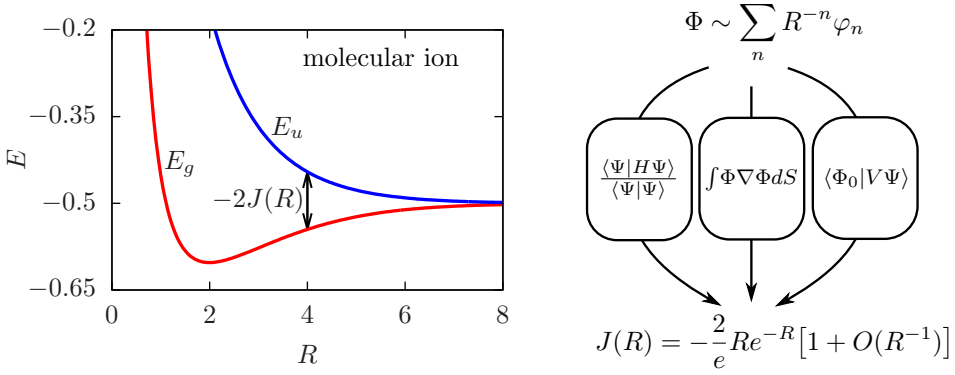

Figure 1. Graphical abstract: The leading term of exchange energy can be calculated from the multipole expansion of the wave function using variational principle, surface integral, or perturbation theory.

Research Article

Convergence properties of the multipole expansion of the exchange contribution to the interaction energy†

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The conventional surface integral formula $J_{\rm surf}[\Phi]$ and an alternative volume integral formula $J_{\rm var}[\Phi]$ are used to compute the asymptotic exchange splitting of the interaction energy of the hydrogen atom and a proton employing the primitive function Φ in the form of its truncated multipole expansion. Closed-form formulas are obtained for the asymptotics of $J_{\rm surf}[\Phi_N]$ and $J_{\rm var}[\Phi_N]$, where Φ_N is the multipole expansion of Φ truncated after the $1/R^N$ term, R being the internuclear separation. It is shown that the obtained sequences of approximations converge to the exact results with the rate corresponding to the convergence radius equal to 2 and 4 when the surface and the volume integral formulas are used, respectively. When the multipole expansion of a truncated, Kth order polarization function is used to approximate the primitive function the convergence radius becomes equal to unity in the case of $J_{\rm var}[\Phi]$. At low order the observed convergence of $J_{\rm var}[\Phi_N]$ is, however, geometric and switches to harmonic only at certain value of $N = N_c$ dependent on K. An equation for N_c is derived which very well reproduces the observed K-dependent convergence pattern. The results shed new light on the convergence properties of the conventional SAPT expansion used in applications to many-electron diatomics.

† Dedicated to Professor Andreas Savin on the occasion of his 65 birthday.

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1. Introduction

Energetic effects of noncovalent molecular interactions are very small, compared to the energies of noninteracting subsystems, nevertheless they determine the properties of condensed matter [1, 2] and influence chemical reactivity [3]. The theoretical framework for the understanding of the nature and origin of noncovalent interactions is provided by Symmetry Adapted Perturbation Theory (SAPT) [4, 5], which introduces rigorous decomposition of the interaction energy into electrostatic, induction, dispersion and exchange contributions. At large interatomic distances R the first three of these constituents can be expanded in powers of R^{-1}, leading to the so-called multipole expansion of interaction energy

$$E_{\rm int}(R) \sim \sum_n C_n R^{-n}, \tag{1}$$

with the C_n's coefficients referred to as the van der Waals constants. While the expansion of Eq. (1) is divergent for any R [6, 7], it is known to provide the correct asymptotic representation of $E_{\rm int}(R)$ for large R [8, 9]. From the perspective of the large R asymptotics of $E_{\rm int}$, the exchange effects might seem to be insignificant. However, at intermediate and short distances the importance of the exchange part of $E_{\rm int}$ is hard to overestimate, as it is responsible for the splitting of potential energy curves and for the strong repulsion in the case of interaction of closed-shell atoms when it provides the necessary quenching of the attractive induction and dispersion components of the interaction energy.

The exchange effects are caused by the resonant tunneling of one or more electrons between the interacting systems and are considered to be non-perturbative, that is, an application of the straightforward Rayleigh-Schrödinger perturbation treatment is unable to provide even qualitative description of the exchange contribution to $E_{\rm int}$ [10, 11]. This problem can be circumvented by the symmetry forcing procedure [12], in which the wave function is correctly symmetrized in each order of perturbation theory. Different variants of symmetry forcing lead to different SAPT expansions [12, 13], of which the most important is the Symmetrized Rayleigh-Schrödinger (SRS) perturbation approach [10, 14]. SRS is nowadays routinely applied in studies of noncovalent interactions of many-electron systems [15–18].

The success of SRS approach is somewhat bewildering, as it is based on the so-called polarization approximation (PA), which is the straightforward application of the Rayleigh-Schrödinger (RS) perturbation theory to molecular interactions. PA is known to diverge when at least one of the interacting subsystems has more than two electrons [19–22]. On the other hand, PA converges for H_2^+ and H_2 to the ground state wave function and energy [10, 11, 23]. For large R this convergence is very slow, as the convergence radius of PA exceeds one by a quantity exponentially decaying with R [11, 23–25]. Irrespectively of the ultimate convergence or divergence, PA provides the asymptotic approximation to the primitive function [19] Φ of the interacting system, in the sense that [8, 26]

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

where Ψ_ν is the wave function of the state ν, $\mathcal{A}_\nu$ is the symmetry operator associated with this state, $\Phi^{(K)}$ is the PA wave function computed through the Kth order, and κ equals two if at least one of the interacting subsystems is charged and three if both are neutral.

From the practical point of view it is important to know the limits of validity

and convergence properties of various approaches to calculation of the exchange contribution to $E_{\rm int}$. In this paper we present exact results concerning the rate of convergence of the exchange energy $J(R)$ of the hydrogen molecular ion H_2^+ when computed using the multipole expansion of the primitive wave function. The exchange energy is defined in this context as

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

where E_g and E_u are the Born-Oppenheimer energies of the lowest *gerade* and *ungerade* states, respectively. The H_2^+ ion is particularly suitable for studies of the convergence of exchange effects for two reasons: (*a*) the analysis is simplified by the fact that there are no electron correlation effects involved and (*b*) the asymptotic expansion of $J(R)$ is known exactly for this system [7]. H_2^+ is one of the most important models of the theory of molecular interactions and there is a wealth of analytical results available for this species [7, 13, 27–29]. H_2^+ is also a prototypical double-well system [30, 31]. The asymptotic expansion of exchange energy of H_2^+ can be conveniently written in the form

$$J(R) = \frac{2}{e}\, R e^{-R}(j_0 + j_1\, R^{-1} + j_2\, R^{-2} + \dots), \tag{4}$$

where $j_0 = -1, j_1 = -\frac{1}{2}$, and $j_2 = -\frac{25}{8}$. The higher j_n coefficients can be found in Ref. [7].

The most widely used method of calculating $J(R)$ employs the surface-integral formula $J_{\rm surf}[\Phi]$ given by [32–35]

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

where the primitive function Φ is assumed to be localized in the "left" half of space and M is the median plane dividing the space into "left" and "right" halves. Atomic units ($\hbar = e = m_e = 1$) are used in Eq. (5) and throughout the paper.

Alternatively, the exchange energy can be calculated from the SAPT formula [25]

$$J_{\rm SAPT}[\Phi] = \frac{\langle\varphi_0|VP\Phi\rangle\langle\varphi_0|\Phi\rangle - \langle\varphi_0|V\Phi\rangle\langle\varphi_0|P\Phi\rangle}{\langle\varphi_0|\Phi\rangle^2 - \langle\varphi_0|P\Phi\rangle^2}, \tag{6}$$

where V is the interaction operator, φ_0 is the unperturbed wave function, and P is the operator inverting the electronic coordinates with respect to the midpoint of the internuclear axis. When Φ is approximated by the polarization function $\Phi^{(K)}$ and the r.h.s. of Eq. (6) is expanded in powers of V, one obtains the SRS expansion of the exchange energy through the Kth order.

In our recent work [36] we showed that the exchange energy can be very accurately calculated from the variational principle based formula $J_{\rm var}[\Phi]$

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

where H is the full Hamiltonian of the interacting system. Numerical results illustrating the convergence of $J_{\rm surf}[\Phi]$, $J_{\rm SAPT}[\Phi]$, and $J_{\rm var}[\Phi]$ with respect to the order of multipole expansion used to approximate the primitive wave function Φ were presented in our previous work [36]. By analyzing these numerical results we

have found that the convergence rate of the leading term, j_0, of the asymptotic expansion of Eq. (4) corresponds to the convergence radius equal to 2, 1, and 4 for the surface-integral, SAPT, and variational formula, respectively.

In this communication we shall present a rigorous mathematical derivation of the discovered convergence rates and the corresponding convergence radii (with respect to the order of multipole expansion of Φ) for j_0 calculated from the surface $J_{\rm surf}[\Phi]$ and variational $J_{\rm var}[\Phi]$ expression (in the case of $J_{\rm SAPT}[\Phi]$ such analysis has already been presented in Ref. [36]). Furthermore we derive closed-form formulas for partial sums of the series approximating j_0 and show that these partial sums converge to the correct value $j_0 = -1$. We shall also explain why in the calculations of j_0 using the primitive function approximated by a finite polarization expansion $\Phi^{(K)}$ the convergence is initially geometric but switches to harmonic when the multipole expansion of $\Phi^{(K)}$ is carried out to sufficiently high order.

2. Asymptotic expansion of the polarization wave function

The non-relativistic Born-Oppenheimer Hamiltonian for an interacting system consisting of two molecules A and B decomposes naturally as $H = H_0 + V$, where $H_0 = H_A + H_B$ is the unperturbed part (H_A and H_B being the Hamiltonians of isolated monomers A and B, respectively) and V is the perturbation accounting for the Coulomb interactions between charged particles belonging to different monomers. In the case of H_2^+ the pertinent partitioning of H is

$$H_0 = -\frac{1}{2}\nabla^2 - \frac{1}{r_a}, \qquad V = \frac{1}{R} - \frac{1}{r_b}, \tag{8}$$

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

Polarization approximation is obtained when one applies the usual RS perturbation theory to the above definition of H_0 and V, with the the unperturbed wave function φ_0 taken as the product of the ground state wave functions of isolated subsystems (in case of H_2^+ the unperturbed wave function is the ground state wave function of a hydrogen atom a, $\varphi_0 = 1s_a$). The polarization corrections to energy are given by

$$E^{(k)} = \langle \varphi_0 | V \varphi^{(k-1)} \rangle, \tag{9}$$

whereas the wave function corrections are defined recursively by equations

$$(H_0 - E_0)\varphi^{(k)} = -V\varphi^{(k-1)} + \sum_{m=1}^{k} E^{(m)} \varphi^{(k-m)} \tag{10}$$

and the intermediate normalization condition $\langle \varphi^{(k)} | \varphi_0 \rangle = 0$ holding for $k > 0$. For $k = 0$ we have $\varphi^{(0)} = \varphi_0$. The wave function corrections can be written in a product form, separating the zeroth-order wave function, $\varphi^{(k)} = \varphi_0 f^{(k)}$, where $f^{(0)} = 1$ and for $k \geq 1$ the factors $f^{(k)}$ satisfy the equation [37, 38]

$$-\tfrac{1}{2}\nabla^2 f^{(k)} + \frac{\partial f^{(k)}}{\partial r_a} = -V f^{(k-1)} + \sum_{m=1}^{k} E^{(m)} f^{(k-m)}. \tag{11}$$

When the perturbation V in Eq. (11) is represented by its multipole expansion

$$V \sim V_2\, R^{-2} + V_3\, R^{-3} + V_4\, R^{-4} + \ldots, \tag{12}$$

$$V_n = -r_a^{n-1} P_{n-1}(\cos\theta_a), \tag{13}$$

one obtains the asymptotic expansion for $f^{(k)}$

$$f^{(k)} \sim \sum_n f_n^{(k)}(r_a, \theta_a)\, R^{-n}, \tag{14}$$

where θ_a is the inclination angle of the electron in a coordinate system centered at the nucleus a and $P_l(x)$ is the Legendre polynomial. Using Eq. (11) one can verify that the factors $f_n^{(k)}(r_a, \theta_a)$ are finite order polynomials in r_a and $\cos\theta_a$

$$f_n^{(k)}(r_a, \theta_a) = \sum_m r_a^m \sum_{l=0} t_{nml}^{(k)}\, P_l(\cos\theta_a). \tag{15}$$

such that $m \le n$ and $l \le m$. Eq. (15) may be viewed as an expansion of Eq. (28) of Ref. [36] in powers of the perturbation V [the function f_n in Eq. (28) of Ref. [36] is defined via $\phi_n = f_n \phi_0$; this definition has been erroneously omitted in the line preceding Eq. (28)].

Since $\langle\Phi|\Phi\rangle = 1 + O(R^{-4})$ and $\langle\Phi|H\Phi\rangle = E_0 + O(R^{-4})$ the asymptotically leading term of $J_{\rm var}[\Phi]$, defined by the j_0 coefficient in Eq. (4), can be obtained by considering a simplified formula

$$J^*_{\rm var}[\Phi] = \langle\Phi|(H - E_0)P\Phi\rangle. \tag{16}$$

Evaluation of Eq. (16) with the multipole expansion of the polarization function truncated after the Kth term,

$$\Phi^{(K)} \sim \varphi_0 \sum_n R^{-n} \sum_{k=0}^{K} f_n^{(k)}, \tag{17}$$

leads to a linear combination of integrals

$$\begin{aligned} &\frac{1}{\pi}\int e^{-r_a - r_b} r_a^m r_b^{m'} P_l(\cos\theta_a) P_{l'}(\cos\theta_b) d^3\mathbf{r} = \\ &\quad = 2e^{-R}\frac{(m+1)!(m'+1)!}{(m+m'+3)!} R^{m+m'+2}\big[1 + O(R^{-1})\big]. \end{aligned} \tag{18}$$

The asymptotic formula (18) shows that only the terms with $m = n$ in Eq. (15) contribute to j_0 of the expansion (4). For this reason we will further consider only the dominant, $m = n$ part of $f_n^{(k)}$, denoted $\widetilde{f}_n^{(k)}$, given by

$$\widetilde{f}_n^{(k)} = r_a^n \sum_{l=0} t_{nl}^{(k)}\, P_l(\cos\theta_a), \tag{19}$$

where $t_{nnl}^{(k)}$ has been denoted by $t_{nl}^{(k)}$. Inserting Eqs. (14) and (15) into Eq. (11) and

comparing coefficients at terms proportional to $r_a^{n-1}R^{-n}$ one obtains the relation

$$n\sum_{l=0}^{n-1} t_{nl}^{(k)} P_l(\cos\theta_a) = \sum_{j=0}^{n-2}\sum_{l=0} t_{jl}^{(k-1)} P_l(\cos\theta_a) P_{n-j-1}(\cos\theta_a). \tag{20}$$

In deriving Eq. (20) we took advantage of the fact that $\nabla^2 f^{(k)}$ and the last term in Eq. (11) do not contain terms proportional to $r_a^{n-1}R^{-n}$.

Since the asymptotic value of the integral of Eq. (18) is independent of l and l', the angular dependence of $\widetilde{f}^{(k)}$ does not affect the asymptotic estimate of Eq. (16) and, therefore, has no influence on j_0. In other words, the value of the asymptotically leading term of $J_{\rm var}[\Phi]$ depends only on the values of Φ on the line joining the nuclei a and b, where $P_l(\cos\theta_a) = P_{l'}(\cos\theta_b) = 1$, similarly as it was observed for $J_{\rm SAPT}[\Phi]$ in Ref. [36]. Thus, in the analysis of the convergence properties of approximations to j_0 it is sufficient to calculate the values of the functions $\widetilde{f}_n^{(k)}$ on the line joining the nuclei,

$$\widetilde{f}_n^{(k)}\big|_{\theta_a=0} = t_n^{(k)} r_a^n, \tag{21}$$

where $t_n^{(k)}$ is defined as the sum

$$t_n^{(k)} = \sum_{l=0} t_{nl}^{(k)}. \tag{22}$$

Substituting $\theta_a = 0$ in Eq. (20) we obtain a simple recurrence relation for the $t_n^{(k)}$ coefficients

$$t_n^{(k)} = \frac{1}{n}\sum_{j=2k-2}^{n-2} t_j^{(k-1)} \tag{23}$$

with the initial, $k = 0$ values given by $t_0^{(0)} = 1$ and $t_n^{(0)} = 0$ for $n > 0$. In setting the lower summation limit in Eq. (23) we used the fact that $t_n^{(k)} = 0$ for $n < 2k$. In Eq. (23) and throughout the paper we use the convention that when the lower summation limit is greater than the upper one the sum is zero. Using Eq. (23) it is straightforward to show that

$$t_n^{(k)} = \frac{n-1}{n} t_{n-1}^{(k)} + \frac{1}{n} t_{n-2}^{(k-1)}, \qquad n > 1, \tag{24}$$

which furnishes a fast algorithm for the calculation of $t_n^{(k)}$.

The values of the multipole expansion of $\Phi^{(K)}$, Eq. (17), truncated after R^{-N} term and computed on the line joining the nuclei with $f_n^{(k)}$ replaced by its dominant part $\widetilde{f}_n^{(k)}$, Eq. (19), are given by

$$\widetilde{\Phi}_N^{(K)}\big|_{\theta_a=0} = \varphi_0 \sum_{n=0}^{N} d_n^{(K)} r_a^n\, R^{-n}, \tag{25}$$

where

$$d_n^{(K)} = \sum_{k=0}^{K} t_n^{(k)}. \tag{26}$$

The multipole expansion of the primitive function Φ truncated after R^{-N}, denoted by Φ_N, is

$$\Phi_N = \lim_{K\to\infty} \Phi_N^{(K)} = \varphi_0 \sum_{n=0}^{N} R^{-n} \sum_{k=0}^{[n/2]} f_n^{(k)}, \tag{27}$$

where $[n/2]$ denotes the integral part of $n/2$. The finite upper limit of the k summation in Eq. (27) is a consequence of the fact that $t_n^{(k)} = 0$ for $k > n/2$. The dominant part of Φ_N, denoted by $\widetilde{\Phi}_N$, is defined in the same way as Φ_N except that $f_n^{(k)}$ is replaced by $\widetilde{f}_n^{(k)}$. On the line joining the nuclei the function $\widetilde{\Phi}_N$ is given by Eq. (25) with superscripts (K) omitted and d_n defined by

$$d_n = \lim_{K\to\infty} d_n^{(K)} = \sum_{k=0}^{[n/2]} t_n^{(k)}. \tag{28}$$

We shall now derive a closed-form formula for d_n. This can be done via a recurrence for differences of consecutive d_n's with $n \geq 2$, which using Eqs. (23) and (28) takes the form

$$d_n - d_{n-1} = \sum_{k=1}^{\infty} \left(\frac{1}{n} \sum_{j=2k-2}^{n-2} t_j^{(k-1)} - \frac{1}{n-1} \sum_{j=2k-2}^{n-3} t_j^{(k-1)} \right), \tag{29}$$

where the lower limit of the k summation was set equal to 1 since for $n \geq 1$ the $k = 0$ term does not contribute to the summation in Eq. (28). The summation over k is actually finite and limited by the condition $t_n^{(k)} = 0$ for $k > n/2$.

Extracting the $j = n - 2$ term form the left inner sum and combining the remaining part with the other sum gives

$$d_n - d_{n-1} = \frac{1}{n} \sum_{k=1}^{\infty} \left(t_{n-2}^{(k-1)} - \frac{1}{n-1} \sum_{j=2k-2}^{n-3} t_j^{(k-1)} \right). \tag{30}$$

Comparison with Eqs. (23) and (26) allows to rewrite Eq. (30) as

$$d_n - d_{n-1} = -\frac{1}{n}(d_{n-1} - d_{n-2}), \tag{31}$$

which together with the fact that $d_0 = 1$ and $d_1 = 0$ gives

$$d_n = \sum_{m=0}^{n} \frac{(-1)^m}{m!}. \tag{32}$$

Eq. (32) agrees with Eq. (36) of Ref. [36] obtained using a different derivation, not related to the polarization expansion of the wave function.

One may note that after multiplication by $n!$ the coefficients d_n and $t_n^{(k)}$ have a combinatorial interpretation: $n!\,d_n$ is equal to the so-called derangement number D_n (see Ref. [39] p. 59, Ref. [40] p. 180, and Ref. [41] entry A000166) defined as the number of permutations with no fixed points (ie. permutations in which all elements change places), while $n!\,t_n^{(k)}$ is equal to the associated Stirling number $d(n,k)$, defined as the number of derengements of n elements having exactly k permutation cycles (Ref. [40] p. 256, Ref. [39] p. 73, and Ref. [41] entry A008306).

3. Closed-from expressions for the partial sums and the convergence rates of the multipole expansion of the exchange energy j_0

Approximations to j_0 obtained from $J_{\rm surf}[\Psi]$ and $J_{\rm var}[\Psi]$, where Ψ is any approximation to the primitive function Φ, will be denoted by $j_0^{\rm surf}[\Psi]$ and $j_0^{\rm var}[\Psi]$, respectively. The convergence of these approximations resulting when Ψ is substituted by the multipole expanded polarization function can be characterized with the help of the increment ratios defined as

$$\rho_N^{(K)}(j_0^{\rm surf}) = \frac{j_0^{\rm surf}[\Phi_N^{(K)}] - j_0^{\rm surf}[\Phi_{N-1}^{(K)}]}{j_0^{\rm surf}[\Phi_{N+1}^{(K)}] - j_0^{\rm surf}[\Phi_N^{(K)}]}, \tag{33}$$

where $\Phi_N^{(K)}$ is the multipole expansion of $\Phi^{(K)}$ truncated after the R^{-N} term, cf. Eq. (17). Increment ratios $\rho_N^{(K)}(j_0^{\rm var})$ are defined analogously. The convergence of results obtained when Ψ is substituted by Φ_N will be characterized by the increment rations $\rho_N(j_0^{\rm surf})$ and $\rho_N(j_0^{\rm var})$, defined as in Eq. (33), but with superscripts (K) omitted. Similar convention will be applied to other quantities as well — symbols without the superscript (K) will denote the $K\to\infty$ limits of the corresponding expressions carrying this superscript. It should be noted that the r.h.s. of Eq. (33) remains unchanged if the functions $\Phi_N^{(K)}$ or Φ_N are replaced by $\widetilde{\Phi}_N^{(K)}$ or $\widetilde{\Phi}_N$, respectively.

3.1. *Surface-integral formula*

It has been shown in Ref. [38] that the large R asymptotics of $J_{\rm surf}[\Phi]$ is determined by the value of Φ at the mid-point of the line joining the nuclei. Specifically, if $\Phi = \phi_0\, f(r_a,\theta_a)$ then

$$J_{\rm surf}[\Phi] = -\frac{1}{2} R e^{-R}\,[f(R/2,0)]^2 + O(e^{-R}). \tag{34}$$

Thus, in view of Eq. (25) the asymptotics of $J_{\rm surf}[\Phi_N^{(K)}]$ is determined by the constant

$$j_0^{\rm surf}[\Phi_N^{(K)}] = j_0^{\rm surf}[\widetilde{\Phi}_N^{(K)}] = -\frac{e}{4}\left(r_N^{(K)}\right)^2, \tag{35}$$

where

$$r_N^{(K)} = \sum_{n=0}^{N} \frac{d_n^{(K)}}{2^n}. \tag{36}$$

Using mathematical induction one can easily prove that the $K \to \infty$ limit of $r_N^{(K)}$, denoted by r_N, is given by

$$r_N = 2\, e_N\big(-\tfrac{1}{2}\big) - 2^{-N} d_N, \tag{37}$$

where $e_n(x)$ denotes the exponential sum function

$$e_n(x) = \sum_{m=0}^{n} \frac{x^m}{m!}. \tag{38}$$

Combining Eqs. (35) and (37) one obtains a simple closed-form formula for $j_0^{\rm surf}[\Phi_N]$, that is for the exchange energy determined by partial sums of the multipole expansion of the primitive function:

$$j_0^{\rm surf}[\Phi_N] = -\frac{e}{4}\left[2e_N(-\tfrac{1}{2}) - 2^{-N} d_N\right]^2. \tag{39}$$

Taking the $N \to \infty$ limit we see that the leading, j_0 term in the expansion of Eq. (4) is correctly obtained in this way, i.e,

$$\lim_{N\to\infty} j_0^{\rm surf}[\Phi_N] = -1, \tag{40}$$

in agreement with the results of Ref. [36].

Equation (39) can be compared with the formula for j_0 obtained by Tang et al. [38] using the surface-integral expression and the polarization function $\Phi^{(K)}$. Their Eq. (7.25) can be recast in our notation as follows:

$$\begin{aligned} j_0^{\rm surf}[\Phi^{(K)}] = -\frac{1}{2}\Bigg[1 &+ \sum_{m_1=2}^{\infty} \frac{1}{m_1 2^{m_1}} + \sum_{m_1,m_2=2}^{\infty} \frac{1}{m_1(m_1+m_2)2^{m_1+m_2}} \\ &+ \sum_{m_1,m_2,m_3=2}^{\infty} \frac{1}{m_1(m_1+m_2)(m_1+m_2+m_3)2^{m_1+m_2+m_3}} + \dots\Bigg]^2, \end{aligned} \tag{41}$$

where the terms in the square brackets involving $k$tuple summation originate from the kth order polarization function $\phi^{(k)}$. The last term (not explicitly written) involves the Ktuple summation and originates from $\phi^{(K)}$. Eq. (41) is a sum of terms of increasingly high order in V, each of which is an infinite sum corresponding to the expansion in powers of R^{-1}. On the other hand, Eq. (39) contains only single sums over terms of different order in R^{-1}, each of which is a closed-form sum of contributions of different orders in V.

Knowing the expression for r_N, the increment ratio $\rho_N(j_0^{\rm surf})$, defined by the $K \to \infty$ limit of Eq. (33), can be written in the form

$$\rho_N(j_0^{\rm surf}) = 2\,\frac{d_N}{d_{N+1}}\,\frac{r_N - 2^{-N-1} d_N}{r_N + 2^{-N-2} d_{N+1}}. \tag{42}$$

When $N \to \infty$ the ratio d_N/d_{N+1} is equal to 1 with an error of the order of $1/(N+1)!$ Estimating the remaining factor using Eq. (37) one finds that

$$\rho_N(j_0^{\rm surf}) = 2 - \frac{3}{4\sqrt{e}} 2^{-N} + O(4^{-N}), \tag{43}$$

which is the result discovered numerically in Ref. [36]. We see that the sequence of approximations to j_0 obtained using the surface integral formula and the multipole expansion of the wave function converges like a series with the convergence radius equal to 2. In Sec. 4.1 we show that for finite K the convergence radius corresponding to the sequence $\rho_N^{(K)})(j_0^{\rm surf})$ remains also equal to 2, although the rate of convergence becomes somewhat slower in this case.

Concluding this Subsection it may be remarked that the authors of Ref. [38] were only concerned with the $K \to \infty$ limit of Eq. (41) and did not consider the convergence rate of the obtained series expansions. In fact, this rate cannot be simply inferred from Eq. (41). On the other hand, the convergence rate corresponding to Eq. (39) can be easily obtained and is given by Eq. (43).

3.2. *Variational formula*

In the case of the variational volume-integral formula it is easier to analyse the convergence rate than to obtain a closed-form expression for the partial sum of the corresponding expansion. We therefore start by considering the increment ratio of Eq. (33) first.

3.2.1. Convergence rate of the variational formula

Employing Eqs. (18) and (25) one obtains

$$\frac{2}{e} j_0^{\rm var}[\Phi_N^{(K)}] = \sum_{m_1,m_2=0}^{N} d_{m_1}^{(K)} d_{m_2}^{(K)} G_{m_1,m_2}, \tag{44}$$

where

$$G_{m_1,m_2} = 2\frac{m_1!m_2!(m_1m_2[m_1+m_2+4]-2)}{(m_1+m_2+3)!}. \tag{45}$$

The numerator in Eq. (33) multiplied by $2/e$ can now be written as

$$q_N^{(K)} = 2d_N^{(K)} p_N^{(K)} + \big(d_N^{(K)}\big)^2 G_{N,N}, \tag{46}$$

where

$$p_N^{(K)} = \sum_{m=0}^{N-1} d_m^{(K)} G_{m,N}. \tag{47}$$

A closed-form formula for the the $K \to \infty$ limits of $p_N^{(K)}$, denoted by p_N, can be obtained using the summation by parts formula,

$$\sum_{j=0}^{n} u_j w_j = u_n W_n - \sum_{j=0}^{n-1} \big(u_{j+1} - u_j\big) W_j, \tag{48}$$

where

$$W_j = \sum_{m=0}^{j} w_m. \tag{49}$$

We shall use this formula with $u_j = d_j$ and $w_j = G_{j,N}$. In this case $u_{j+1} - u_j = (-1)^{j+1}/(j+1)!$ and

$$W_j = \frac{2}{(N+1)(N+2)} - 2\big[(j+1)(N+5) + j^2\big]\frac{(j+1)!N!}{(N+j+3)!}. \tag{50}$$

The latter identity can be proved with mathematical induction. The evaluation of the summation on the r.h.s. of Eq. (48) reduces now to sums of the form

$$F^s_{m,n} = \sum_{j=0}^{n} \frac{(-1)^j j^s}{(j+m)!}, \tag{51}$$

where m and s are non-negative integers. For $s = 0$ $F^0_{n,m} = (-1)^m(d_{n+m} - d_{m-1})$ while for $s > 0$ one easily obtains the recurrence relation

$$F^s_{m,n} = F^{s-1}_{m-1,n} - mF^{s-1}_{m,n}. \tag{52}$$

The latter relation allows us to express p_N in the closed form as

$$p_N = \frac{(-1)^N N!}{(2N+1)!} - d_N\frac{(N!)^2}{(2N)!}. \tag{53}$$

Therefore the $K \to \infty$ limit of $q^{(K)}_N$, denoted by q_N, is

$$q_N = -4d_N^2(3N+4)\frac{[(N+1)!]^2}{(2N+3)!} + 2d_N\frac{(-1)^N N!}{(2N+1)!}, \tag{54}$$

and consequently

$$\rho_N(j_0^{\rm var}) = 4 - 2N^{-1} + O(N^{-2}), \tag{55}$$

in agreement with the numerical results of Ref. [36]. Thus, the series of approximations to the exchange energy j_0 obtained from the multipole expansion of the primitive function and the variational formula converges at large N like a geometric series with the term ratio equal to 4. In Section 4 we shall show that, surprisingly enough, this convergence changes to harmonic when K is finite, i.e., when Φ is replaced with its approximation by a finite-order polarization function $\Phi^{(K)}_N$.

3.2.2. Partial sums for the variational formula

Recalling the definition of q_N as the numerator of Eq. (33) times $2/e$ one can easily see that the constant j_0 calculated from the variational formula with the multipole expansion of the primitive function through the $1/R^N$ terms can be obtained by summing the q_j increments up to $j = N$. Using Eq. (54) one finds

$$\frac{2}{e}j_0^{\rm var}[\Phi_N] = \sum_{j=0}^{N} q_j = Q_N + L_N, \tag{56}$$

where the j summation in Eq. (56) was separated into the Q_N contribution containing terms quadratic in d_j^2 and the L_N part linear in d_j. Both these sums can be

calculated using the summation by parts formula of Eq. (48). The Q_N sum is obtained from this formula by setting $u_j = -4d_j^2$ and $w_j = (3j+4)[(j+1)!]^2/(2j+3)!$ The differences of u_j's are then given by $u_{j+1} - u_j = \alpha_j + \beta_j$, where

$$\alpha_j = 8\, d_j\, \frac{(-1)^j}{(j+1)!}, \qquad \beta_j = -4\, \frac{1}{[(j+1)!]^2}. \tag{57}$$

The sums $w_0 + \cdots + w_j$ can be proved with the mathematical induction to be equal to $W_j = 1 + \gamma_j$, where

$$\gamma_j = -2\, \frac{[(j+2)!]^2}{(2j+4)!}. \tag{58}$$

The summation formula of Eq. (48) gives now

$$Q_N = -4 - 4\, d_N^2\, \gamma_N - \sum_{j=0}^{N-1} (\alpha_j + \beta_j)\, \gamma_j. \tag{59}$$

Using the definitions of α_j and γ_j the L_N term in Eq. (56) can be written in the form

$$L_N = \sum_{j=0}^{N-1} u_j w_j + \sum_{j=0}^{N-1} \alpha_j \gamma_j + 2 d_N \frac{(-1)^N N!}{(2N+1)!} \tag{60}$$

where now we have set $u_j = d_j$ and

$$w_j = 2 \frac{4j+7}{2j+3} \frac{(-1)^j j!}{(2j+1)!}. \tag{61}$$

Note that the sums containing $\alpha_j \gamma_j$ cancel out when the sum $Q_N + L_N$ is taken. To execute the first sum on the r.h.s. of Eq. (60) using the summation by parts formula we need an expression for the sums $W_j = w_0 + \cdots + w_j$. With the help of the mathematical induction we find that $W_j = 4 + \delta_j$, where

$$\delta_j = 4(-1)^j \frac{(j+1)!}{(2j+3)!}. \tag{62}$$

Application of the summation by parts formula to the first term in Eq (60) gives

$$\sum_{j=0}^{N-1} u_j w_j = 4 + u_{N-1} \delta_{N-1} - \sum_{j=0}^{N-2} (u_{j+1} - u_j) \delta_j. \tag{63}$$

Now the only contributions to $j_0^{\rm var}[\Phi_N]$ that still have to summed are the sum of $\beta_j \gamma_j$ in Eq. (59) and the sum on the r.h.s. of (63). These sums can be combined to yield

$$\sum_{j=0}^{N-2} \left[\beta_j \gamma_j + (u_{j+1} - u_j) \delta_j \right] = 2 d_{2N-1}. \tag{64}$$

Using this result we obtain the desired closed form expression

$$\frac{2}{e}j_0^{\rm var}[\Phi_N] = -2d_{2N} + \frac{2}{(2N+1)!} - 2\frac{(-1)^N N!}{(2N+1)!}d_N + 8\frac{[(N+2)!]^2}{(2N+4)!}d_N^2. \tag{65}$$

It is readily seen that the $N \to \infty$ limit of this formula, resulting from the first term on the r.h.s., is equal to $-2/e$ in agreement with the exact value $j_0 = -1$. After some manipulations one can also verify that the corresponding increment ratio of Eq. (33) agrees with the estimate of Eq. (55).

4. Convergence rate in the case of truncated polarization expansion

4.1. *The surface-integral formula*

When K is finite the increment ratio of Eq. (33) takes the form

$$\rho_N^{(K)}(j_0^{\rm surf}) = A_N^{(K)} B_N^{(K)}, \tag{66}$$

where $A_N^{(K)} = d_N^{(K)}/d_{N+1}^{(K)}$ and

$$B_N^{(K)} = 2\frac{r_N^{(K)} - 2^{-N-1}d_N^{(K)}}{r_N^{(K)} + 2^{-N-2}d_{N+1}^{(K)}}. \tag{67}$$

Equation (67) may be regarded a finite K precursor of Eq. (42). In view of Eq. (A9) the asymptotics of $A_N^{(K)}$ is given by

$$A_N^{(K)} = 1 + N^{-1} - (K-1)N^{-1}(\ln N)^{-1} + O\big(N^{-1}(\ln N)^{-2}\big). \tag{68}$$

After expanding Eq. (67) one obtains the following asymptotic expression for $B_N^{(K)}$

$$B_N^{(K)} = 2 - c_N^{(K)}2^{-N} + O(4^{-N}), \tag{69}$$

where

$$c_N^{(K)} = \frac{2d_N^{(K)} + d_{N+1}^{(K)}}{2r_N^{(K)}}. \tag{70}$$

Equation (36) shows that $r_N^{(K)}$ is a sum of rapidly decaying terms, and therefore converges quickly to its limit. Specifically it can be showed that for $N > 2K+1$

$$r_{2K+1} \le r_N^{(K)} \le r_N \tag{71}$$

and

$$r_N^{(K)} = 2e_{2K+1}(-\tfrac{1}{2}) + O(2^{-2K}). \tag{72}$$

For this reason asymptotics of $c_N^{(K)}$ is determined by the large N behavior of

$d_N^{(K)}$. Eq. (A9) implies then that at large N and fixed K we have

$$c_N^{(K)} = \frac{3(\ln N)^{K-1}}{4e_{2K+1}(-\frac{1}{2})(K-1)!N}\big[1 + O((\ln N)^{-1})\big]. \tag{73}$$

The $N \to \infty$ limit of $c_N^{(K)}$ (with fixed K) is therefore

$$\lim_{N\to\infty} c_N^{(K)} = 0. \tag{74}$$

On the other hand the $K \to \infty$ limit of $c_N^{(K)}$ for a fixed N is

$$c_N = \lim_{K\to\infty} c_N^{(K)} = \frac{3d_N}{2r_N}\big[1 + O((N!)^{-1})\big]. \tag{75}$$

Ultimately the limit of c_N is

$$\lim_{N\to\infty} c_N = \frac{3}{4\sqrt{e}}, \tag{76}$$

in agreement with Eq. (43). Note that the combined limit $K \to \infty, N \to \infty$ of $c_N^{(K)}$ does not exist, as the result depends on the order of limits.

The asymptotics of the increment ratio of $j_0^{\mathrm{surf}}[\Phi_N^{(K)}]$ is given by

$$\rho_N^{(K)}(j_0^{\mathrm{surf}}) = 2 + 2N^{-1} - 2(K-1)N^{-1}(\ln N)^{-1} + O\big(N^{-1}(\ln N)^{-2}\big). \tag{77}$$

Eq. (77) agrees with the results presented for $K = 1$ in Ref. [36]. This equation shows that for finite K the convergence radius corresponding to $\rho_N^{(K)}(j_0^{\mathrm{surf}})$ and equal 2 is the same as for $K = \infty$. It may seem disturbing that the $K \to \infty$ limit of Eq. (77) does not coincide with Eq. (43). This apparent inconsistency results from the facts that the $K \to \infty$ and $N \to \infty$ limits of $\rho_N^{(K)}(j_0^{\mathrm{surf}})$ do not commute.

4.2. *The variational formula*

In this subsection we shall show that for finite K the convergence of of $\rho_N^{(K)}(j_0^{\mathrm{var}})$ corresponds to the convergence radius of 1, i.e. becomes harmonic, in contrast to the fast geometric convergence found for $K = \infty$.

The inverse d'Alembert ratio $\rho_N^{(K)}(j_0^{\mathrm{var}})$ can be factored as

$$\rho_N^{(K)}(j_0^{\mathrm{var}}) = A_N^{(K)} D_N^{(K)}, \tag{78}$$

similarly to Eq. (66) for the surface-integral formula. $D_N^{(K)}$ is defined as

$$D_N^{(K)} = \frac{2p_N^{(K)} + d_N^{(K)} G_{N,N}}{2p_{N+1}^{(K)} + d_{N+1}^{(K)} G_{N+1,N+1}}. \tag{79}$$

As $d_N^{(K)} = d_N$ for $N \leq 2K+1$ we have

$$p_N^{(K)} - p_N = \sum_{m=2K+2}^{N-1} \big(d_m^{(K)} - d_m\big) G_{m,N}. \tag{80}$$

Since

$$\frac{G_{m,N}}{G_{m+1,N}} = \frac{mN}{(m+1)^2}\big[1 + O(N^{-1})\big] \tag{81}$$

the $m = 2K+2$ term asymptotically dominates the sum in Eq. (80),

$$p_N^{(K)} - p_N = g_N^{(K)}\big[1 + O(N^{-1})\big], \tag{82}$$

where we have defined

$$g_N^{(K)} = \big(d_{2K+2}^{(K)} - d_{2K+2}\big) G_{2K+2,N}. \tag{83}$$

Comparison with Eq. (28) shows that

$$g_N^{(K)} = -t_{2K+2}^{(K+1)} G_{2K+2,N}. \tag{84}$$

From Eq. (23) we see that

$$t_{2k}^{(k)} = \frac{1}{2k} t_{2k-2}^{(k-1)} = \frac{1}{(2k)!!}, \tag{85}$$

therefore

$$g_N^{(K)} = -\frac{G_{2K+2,N}}{(2K+2)!!}. \tag{86}$$

Stirling's approximation shows that $G_{N,N} = O(\sqrt{N} 2^{-2N})$, thus

$$D_N^{(K)} = \frac{p_N - g_N^{(K)}}{p_{N+1} - g_{N+1}^{(K)}}\big[1 + O(N^{-1})\big]. \tag{87}$$

The switching of the convergence rate of $j_0^{\mathrm{var}}[\Phi_N^{(K)}]$ is caused by the change of relative importance of p_N and $g_N^{(K)}$, as the ratios of consecutive elements of these sequences are

$$\frac{p_N}{p_{N+1}} = 4 - 2N^{-1} + O(N^{-2}), \tag{88}$$

and

$$\frac{g_N^{(K)}}{g_{N+1}^{(K)}} = 1 + (2K+3)N^{-1} + O(N^{-2}). \tag{89}$$

This switching phenomenon is illustrated in Fig. 2.

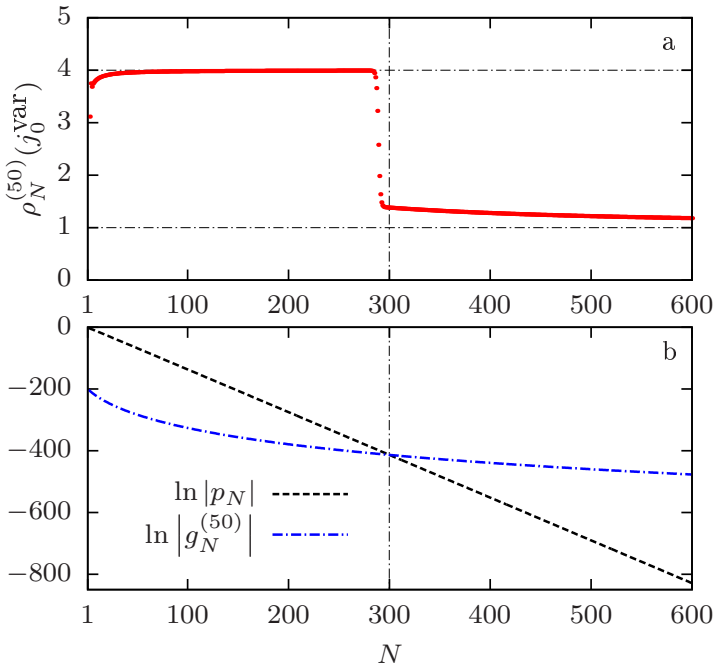

Figure 2. Switching of convergence rate in $\rho_N^{(50)}(j_0^{(\rm var)})$.

The change of convergence pattern, observed numerically in Ref. [36], takes place for $N = N_c$, where N_c is given as a solution of $|p_{N_c}| \approx |g_{N_c}^{(K)}|$, which means that asymptotically

$$\frac{\Gamma(N_c)\Gamma(N_c+2K+5)}{\Gamma(2N_c+1)} = 2e\frac{(2K+2)!}{(2K)!!}. \tag{90}$$

Equation (90) is slightly different from Eq. (59) of our previous work, Ref. [36], which contains a numerical error. However, the solutions N_c of both equations are asymptotically equal for large K. These solutions differ by less than 0.5% already for $K = 40$ and agree very well with the numerically observed values [36]. Stirling's approximation applied to both sides of Eq. (90) shows that asymptotically

$$N_c \sim K \ln K. \tag{91}$$

Equations (78) and (89) show that for $N > N_c$ the increment ratio for $j_0^{\rm var}[\Phi_N^{(K)}]$ behaves as

$$\rho_N^{(K)}(j_0^{\rm var}) = 1 + (2K+4)N^{-1} + (K-1)N^{-1}(\ln N)^{-1} + O(N^{-1}(\ln N)^{-2}), \tag{92}$$

confirming the numerical results of Ref. [36]. The fact that the $K \to \infty$ limit of Eq. (92) does not coincide with Eq. (55) results from the fact that the $K \to \infty$ and $N \to \infty$ limits of $\rho_N^{(K)}(j_0^{\rm var})$ do not commute.

5. Summary and conclusions

Using the molecular hydrogen ion as a model system we have analytically investigated the applicability of the conventional multipole expansion of the wave function

to obtain the large-R asymptotics of the exchange contribution to the interaction energy. We considered the well-known surface integral formula as well as the volume-integral formula derived from the variational principle. We have obtained closed-form expressions for partial sums of the corresponding sequences of approximations to the constant j_0 characterizing the exponential fall off of the exchange energy. Furthermore, we obtained analytical expressions for the large-N behavior, N being the maximal oder of the multiple expansion included, of the increment rations of the considered approximations to j_0. These partial sums converge to the correct limit $j_0 = -1$ for both investigated formulas (for the conventional SAPT formula this was proven in Ref. [36]). The variational formula is characterized by a remarkably fast convergence, matching that of a geometric series with the quotient $= \frac{1}{4}$ (or, equivalently, having the convergence radius $\rho = 4$). This convergence is much faster than that resulting from the application of the conventional SAPT formula [36]. In the case of the surface-integral formula we observed slightly slower convergence, namely that of a geometric series with the quotient $q = \frac{1}{2}$ (or $\rho = 2$). We have also demonstrated a peculiar switching from geometric to harmonic convergence in the case of calculations based on the variational formula and the multipole expansion of a truncated polarization function. In this case for $N < N_c$, where N_c is a certain critical value of N, the increment ratios behave like $4 - 2N^{-1}$, whereas for $N > N_c$ its leading term changes to unity and the sub-leading term depends on the order of the polarization function, K. The critical value N_c is roughly five or six times greater than K for K less than 100 and grows as $K \ln K$ for large K. In the case of the surface-integral formula we do not observe a similar change of the convergence rate when a finite-order polarization expansion is used to approximate Φ.

Our analytic results show that the variational volume integral formula offers a considerable advantage, compared to the standard SAPT formula, in computing the exchange contribution to the interaction energy using the conventional multpole and/or basis set expansion of the wave function. This observation suggest a possibility of a significant improvement over the conventional SAPT approach to the problem of molecular interactions, both in terms of the convergence with respect to the order of the interaction potential and the basis set size.

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Appendix A. Asymptotics of wave function coefficients

In this Appendix we shall show that the wave function coefficients $t_n^{(k)}$ behave at large n as

$$t_n^{(k)} = \frac{(\ln n)^{k-1}}{n(k-1)!}\left[1 + O\left(\frac{1}{\ln n}\right)\right]. \tag{A1}$$

For $k = 1$ and $k = 2$ the non-zero values of $t_n^{(k)}$ are

$$\begin{aligned} t_n^{(1)} &= \frac{1}{n}, \quad n \geq 2, \\ t_n^{(2)} &= \frac{H_{n-2}}{n} - \frac{1}{n}, \quad n \geq 4, \end{aligned} \tag{A2}$$

where H_n are the harmonic numbers

$$H_n = \sum_{k=1}^{n} \frac{1}{k} \tag{A3}$$

growing asymptotically as $H_n = \ln n + \gamma + O(n^{-1})$, where $\gamma = 0.577215...$ is the Euler-Mascheroni constant. The non-zero values of $t_n^{(3)}$, obtained for $n \geq 6$, are given by a more complicated expression,

$$t_n^{(3)} = \frac{H_{n-2}^2}{2n} - \frac{H_{n-2}}{n} + \frac{1}{n}\left(-\frac{1}{3} + H_3 - \frac{1}{2}H_3^2 \right) + \frac{1}{n(n-2)} - \frac{1}{2n}\sum_{m=4}^{n-2} \frac{1}{m^2}, \tag{A4}$$

with the first term on the r.h.s. determining the large n asymptotics of $t_n^{(3)}$. One can show that the large n asymptotics of $t_n^{(k)}$ is determined by the application of the recurrence relation (23) to the leading term of $t_n^{(k-1)}$. This is a consequence of the relation

$$\sum_{j=m}^{n} \frac{H_j^p}{j} = \frac{H_n^{p+1} - H_{m-1}^{p+1}}{p+1} + O(H_n^{p-1}), \tag{A5}$$

which is analogue of the integral formula

$$\int_m^n \frac{(\ln x)^p}{x} dx = \frac{(\ln n)^{p+1} - (\ln m)^{p+1}}{p+1}. \tag{A6}$$

To prove Eq. (A5) one can use the summation by parts formula of Eq. (48) with $u_j = H_j^p$, $w_j = j^{-1}$, and $W_j = H_j$. One obtains then

$$\begin{aligned} \sum_{j=m}^{n} \frac{H_j^p}{j} &= \frac{H_n^{p+1} - H_{m-1}^{p+1}}{p+1} \\ &- \frac{p}{p+1} \sum_{q=1}^{p} (-1)^q \binom{p}{q} \sum_{j=m}^{n} \frac{H_j^{p-q}}{j^{q+1}} \\ &- \frac{1}{p+1} \sum_{q=2}^{p} \binom{p}{q} \sum_{j=m-1}^{n-1} \frac{H_j^{p-q+1}}{(j+1)^q}. \end{aligned} \tag{A7}$$

The sub-dominant contributions to this sum can be bounded by the inequalities

$$\sum_{j=m}^{n} \frac{H_j^p}{j^q} \leq H_n^p \sum_{j=m}^{n} \frac{1}{j^q} \leq \zeta(q) H_n^p, \tag{A8}$$

where $q > 1$ and $\zeta(s)$ is the Riemann zeta function. Employing the relation (A5) while executing the recurrence (23) and replacing H_n by $\ln n$ one obtains Eq. (A1). It is easy to see that the cumulative coefficients $d_N^{(K)}$ obtained by performing the

summation of $t_n^{(k)}$ over k behave essentially in the same way as $t_n^{(k)}$

$$d_N^{(K)} = \frac{(\ln N)^{K-1}}{N(K-1)!}\left[+ O\left((\ln N)^{-1} \right)\right]. \tag{A9}$$

Note that the $N \to \infty$ limit (with K fixed) of $d_N^{(K)}$ is zero. However, for large K the values of $d_N^{(K)}$ are very close to $1/e$ for a quite broad range of N. For instance $1/e - d_N^{(20)}$=1.3×10^{-14}, 7.3×10^{-8}, 3.3×10^{-5}, and 1.0×10^{-3} for $N = 10^2$, 10^3, 10^4, and 10^5, respectively.