

Introduction

Exchange energy is defined as the difference of the Born-Oppenheimer electronic energies of the lowest two states of a diatomic molecule with one or two active electrons,

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

Exchange energy is relevant experimentally in the studies of atmospheric and interstellar chemistry and affects the interaction potentials used in the research on the cold atoms and molecules. The exchange energy of H_2^+ provides an important benchmark of the theory of molecular interactions.

The Hamiltonian of the molecular ion H_2^+ can be decomposed as $H = H_0 + V$ with

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

where r_a and r_b are the distances of the electron to the nuclei a and b , and R is the interatomic distance. The H_2^+ exchange energy has the following large- R asymptotic form [1]

$$J(R) = 2e^{-R-1}R(j_0 + j_1R^{-1} + j_2R^{-2} + \dots), \quad (3)$$

where $j_0 = -1, j_1 = -\frac{1}{2}, j_2 = \frac{25}{8}$, etc.

The three formulas for $J(R)$

The surface-integral formula of Holstein [2] and Herring [3] is

$$J_{\text{surf}}[\varphi] = \frac{\int_M \varphi \nabla \varphi d\mathbf{S}}{\langle \varphi | \varphi \rangle - 2 \int_{\text{right}} \varphi^2 dV}. \quad (4)$$

The formula based on the Symmetry Adapted Perturbation Theory is [4]

$$J_{\text{SAPT}}[\varphi] = \frac{\langle \varphi_0 | VP\varphi \rangle \langle \varphi_0 | \varphi \rangle - \langle \varphi_0 | V\varphi \rangle \langle \varphi_0 | P\varphi \rangle}{\langle \varphi_0 | \varphi \rangle^2 - \langle \varphi_0 | P\varphi \rangle^2}. \quad (5)$$

The third formula can be derived from the Rayleigh-Ritz functional,

$$J_{\text{var}}[\varphi] = \frac{\langle \varphi | HP\varphi \rangle \langle \varphi | \varphi \rangle - \langle \varphi | H\varphi \rangle \langle \varphi | P\varphi \rangle}{\langle \varphi | \varphi \rangle^2 - \langle \varphi | P\varphi \rangle^2}. \quad (6)$$

In the above formulas P is the operator inverting the electronic coordinates with respect to the center of symmetry of H_2^+ , and M is the median plane of this ion.

Multipole expansion of the wave function

The multipole expansion of the interaction potential V is

$$V \sim R^{-2}V_2 + R^{-3}V_3 + R^{-4}V_4 + \dots, \quad V_n = -r_a^{n-1}P_{n-1}(\cos\theta_a). \quad (7)$$

The primitive function φ can be approximated by the partial sum of the multipole corrections,

$$\Phi_N = \sum_{n=0}^N \varphi_n R^{-n}. \quad (8)$$

The van der Waals coefficients C_n and the multipole corrections to the wave function, φ_n , are given by the following recurrence:

$$C_n = \sum_{m=2}^n \langle \varphi_0 | V_m \varphi_{n-m} \rangle, \quad (H_0 - E_0)\varphi_n = \sum_{m=2}^n (C_m - V_m)\varphi_{n-m}. \quad (9)$$

The dominant contributions to φ_n sufficient to calculate j_0 are [6,7]

$$\tilde{\varphi}_n = \varphi_0 d_n r_a^n \quad \text{with} \quad d_n = \sum_{m=0}^n \frac{(-1)^m}{m!}. \quad (10)$$

The convergence rates

$$\rho_N(j_0^{\text{surf}}) = \frac{j_0^{\text{surf}}[\Phi_N] - j_0^{\text{surf}}[\Phi_{N-1}]}{j_0^{\text{surf}}[\Phi_{N+1}] - j_0^{\text{surf}}[\Phi_N]} \quad (11)$$

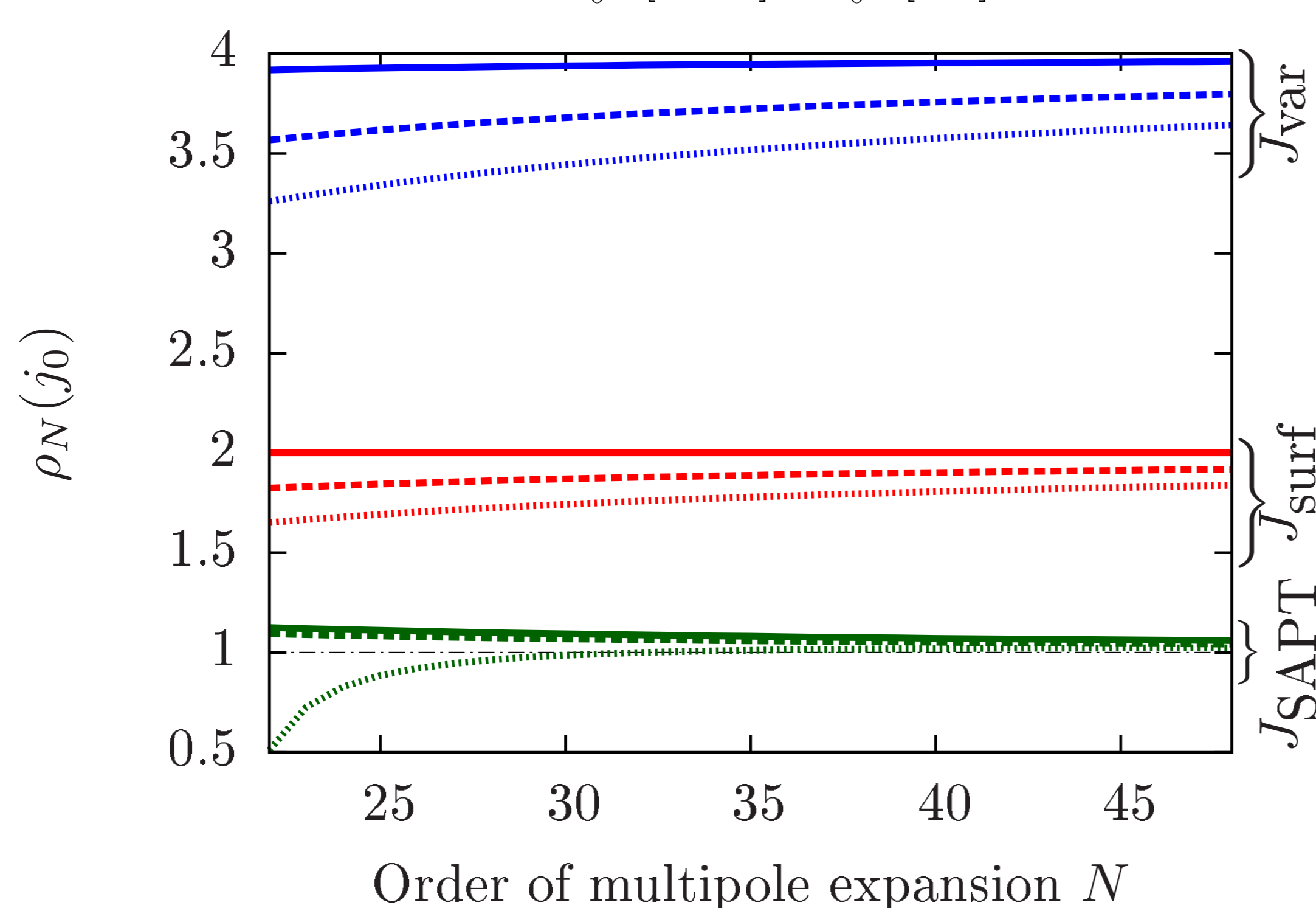


Figure 1: Convergence radii ρ_N calculated for j_0 (solid lines), j_1 (dashed lines) and j_2 (dotted lines) obtained from $J_{\text{var}}[\varphi_N]$, $J_{\text{surf}}[\varphi_N]$ and $J_{\text{SAPT}}[\varphi_N]$.

$$\rho_N(j_0^{\text{var}}) = 4 - 2N^{-1} + O(N^{-2}) \quad (12)$$

$$\rho_N(j_0^{\text{surf}}) = 2 - \frac{3}{4\sqrt{e}}2^{-N} + O(4^{-N}) \quad (13)$$

$$\rho_N(j_0^{\text{SAPT}}) = 1 + 3N^{-1} + O(N^{-2}) \quad (14)$$

Partial sums of exchange energy

$$\frac{2}{e}j_0^{\text{SAPT}}[\Phi_N] = -2d_{N+3} + \frac{2d_{N+1}}{(N+2)(N+3)} \quad (15)$$

$$\frac{2}{e}j_0^{\text{surf}}[\Phi_N] = -\frac{1}{2} \left[2 \sum_{m=0}^N \frac{(-1)^m}{2^m m!} - 2^{-N} d_N \right]^2 \quad (16)$$

$$\frac{2}{e}j_0^{\text{var}}[\Phi_N] = -2d_{2N} + \frac{2}{(2N+1)!} - 2 \frac{(-1)^N N!}{(2N+1)!} d_N + 8 \frac{[(N+2)!]^2}{(2N+4)!} d_N^2 \quad (17)$$

In all three cases the correct value of $j_0 = -1$ is obtained in the $n \rightarrow \infty$ limit, as

$$\lim_{N \rightarrow \infty} d_N = \sum_{m=0}^{\infty} \frac{(-1)^m}{m!} = \frac{1}{e}. \quad (18)$$

In the case of the surface-integral formula this result has already been proved in Ref. [5].

Numerical results

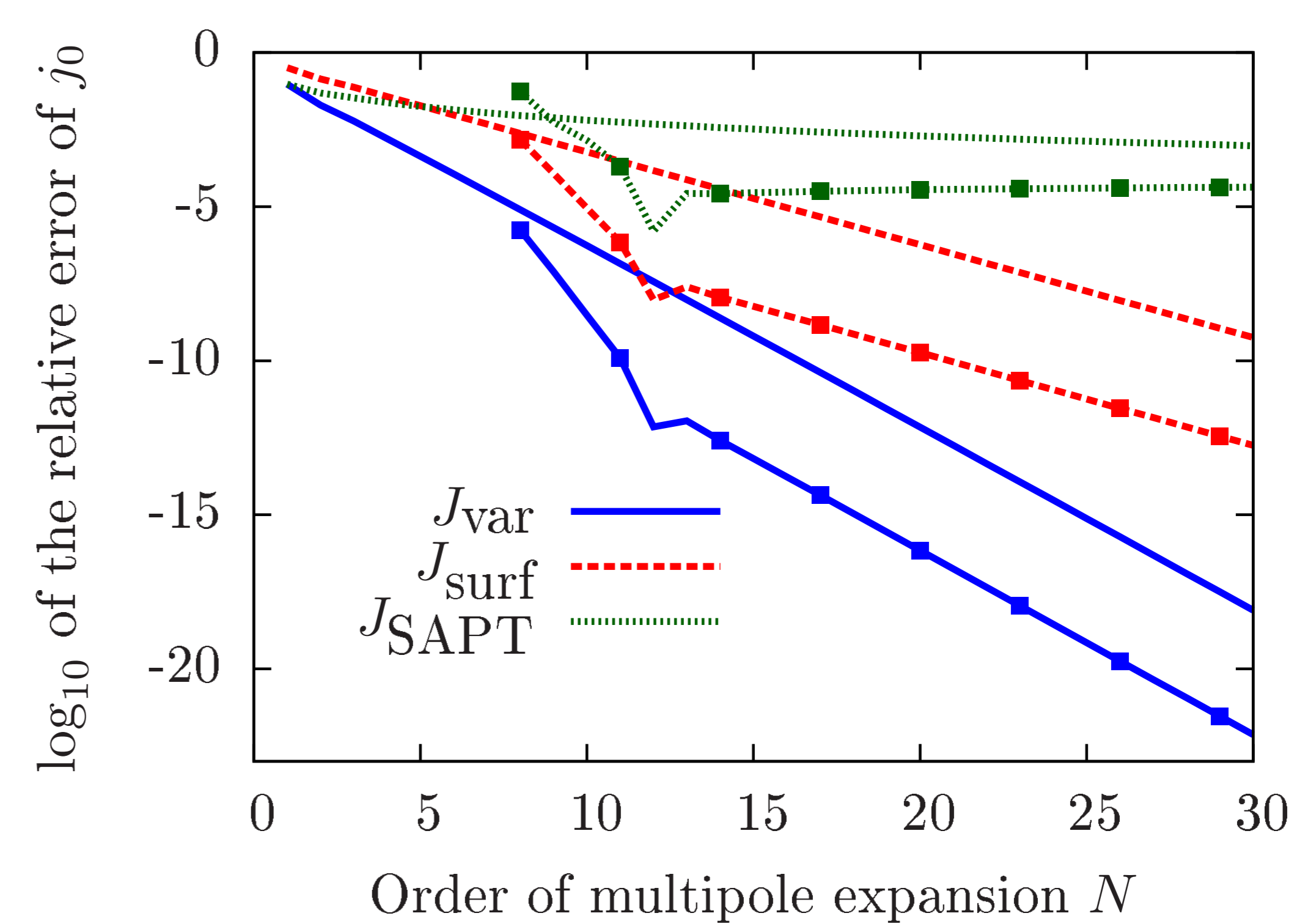


Figure 2: Convergence of the j_0 term of the asymptotic expansion of $J(R)$ obtained from the multipole expansion of the primitive function. Lines with squares indicate values obtained from eight-term Levin- u extrapolation.

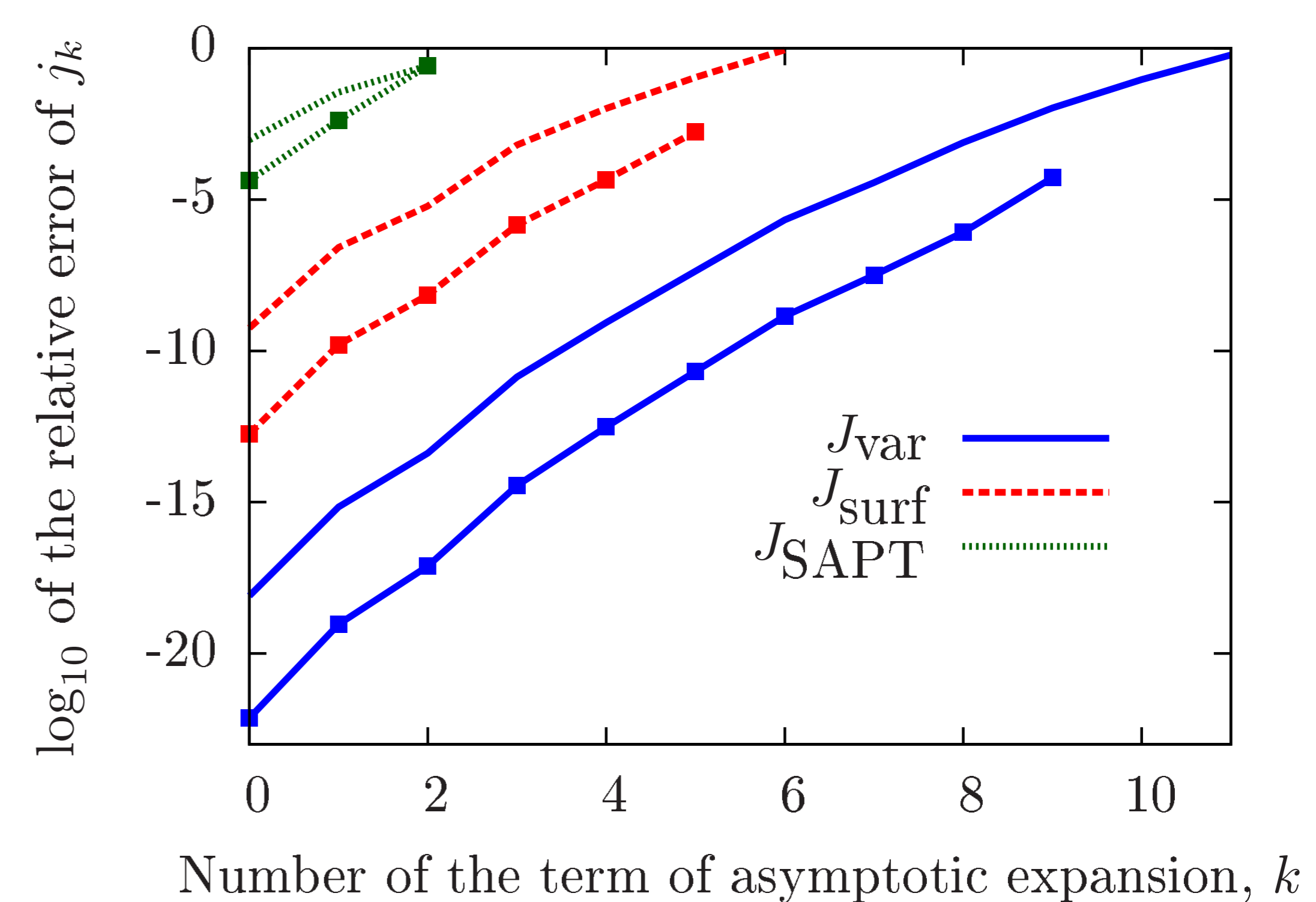


Figure 3: Accuracy of the j_k coefficients in the asymptotic expansion of $J(R)$ calculated using the multipole expansion of the primitive function Φ_N of Eq. (8) with $N=30$. Lines with squares indicate values obtained from eight-term Levin- u extrapolation.

Conclusions

The convergence properties of the variational formula are much superior to the other two approaches, as the convergence rates are 4, 2 and 1 for $j_0^{\text{var}}[\Phi_N]$, $j_0^{\text{surf}}[\Phi_N]$, and $j_0^{\text{SAPT}}[\Phi_N]$, respectively.

Our ongoing work focuses on the incorporation of the variational formula into the general theory of molecular interactions. Preliminary results are very encouraging.

References

- [1] J. Čížek, R. J. Damburg, S. Graffi, *et al.*, *Phys. Rev. A*, **33**, 12 (1986)
- [2] T. Holstein, *J. Phys. Chem.*, **56**, 832 (1952)
- [3] C. Herring, *Rev. Mod. Phys.*, **34**, 631 (1962)
- [4] P. Gniewek, B. Jeziorski, *Phys. Rev. A*, **90**, 022506 (2014)
- [5] K. T. Tang, J. P. Toennies, and C. L. Yiu, *J. Chem. Phys.*, **94**, 7266 (1991)
- [6] P. Gniewek, B. Jeziorski, accepted in *J. Chem. Phys.* (2015), arxiv:1507.02121
- [7] P. Gniewek and B. Jeziorski, manuscript in preparation (2015)

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