Calculation of the exchange splitting of the interaction energy of $H_2^+$ based on the multipole expansion of the wave function

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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,

$$J(R) = \frac{1}{2}[E(R) - E(0)] \tag{1}$$

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 $H = H_a + V$ with

$$H_a = \frac{1}{2} \rho N \left( \frac{1}{r_a} + \frac{1}{r_b} \right)$$
$$V = \frac{1}{R} \left( \frac{1}{r_a} + \frac{1}{r_b} \right)$$ \tag{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]

$$J(R) = 2e^{-R} R(J_b + J_3 R + J_3 R^2 + \ldots) \tag{3}$$

where $J_b = -1, J_3 = -\frac{3}{8}$, etc.

The three formulas for $J(R)$

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

$$J_{\text{surf}}[\bar{\varphi}] = \int_0^\infty \rho N \phi^2 d\bar{R} \tag{4}$$

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

$$J_{\text{SAPT}}[\bar{\varphi}] = \frac{\langle \rho^2 | V^2 | \rho^2 \rangle}{\langle \rho^2 | \phi^2 | \rho^2 \rangle} - \frac{\langle \rho^2 | V^2 | \rho^2 \rangle}{\langle \phi^2 | \phi^2 \rangle} \tag{5}$$

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

$$J_{\text{var}}[\bar{\varphi}] = \frac{\langle \phi^2 | H^2 | \phi^2 \rangle}{\langle \phi^2 | \phi^2 \rangle} - \frac{\langle \rho^2 | \phi^2 | \rho^2 \rangle}{\langle \phi^2 | \phi^2 \rangle} \tag{6}$$

In the above formulas $P$ is the operator inverting the electronic coordinates with respect to the center 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

$$V \sim R^{-2} V_2 + R^{-3} V_3 + R^{-4} V_4 + \ldots, \quad V_0 = -e^2\phi_0^2 |P_{n-1}|(\cos \theta_0). \tag{7}$$

The primitive function $\varphi$ can be approximated by the partial sum of the multipole corrections,

$$\Phi_N = \sum_{n=2}^N \varphi_n R^{-n} \tag{8}$$

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

$$C_n = \sum_{n=2}^{N} \langle \rho^2 | V \rho \varphi_n \rangle, \quad (H_0 - E_0) \varphi_n = \sum_{n=2}^{N} (C_n - V_0) \varphi_n. \tag{9}$$

The dominant contributions to $\varphi_n$ sufficient to calculate $J_b$ are [6,7]

$$\varphi_n = \varphi_n d_n r_b^{-n} \tag{10}$$

The convergence rates

$$\rho_N(j_0) = \frac{\rho_{N\text{surf}}[\bar{\varphi}]}{\rho_{N\text{surf}}[\bar{\varphi}]}, \quad \rho_N(j_{0\text{var}}) = \frac{\rho_{N\text{var}}[\bar{\varphi}]}{\rho_{N\text{surf}}[\bar{\varphi}]}, \quad \rho_N(j_{0\text{SAPT}}) = \frac{\rho_{N\text{SAPT}}[\bar{\varphi}]}{\rho_{N\text{surf}}[\bar{\varphi}]} \tag{11}$$

Partial sums of exchange energy

$$\frac{2}{\beta_{\text{surf}}}[\bar{\varphi}] = -2d_{N+1} + \frac{2d_{N+1}}{N+2} \tag{15}$$

$$\frac{2}{\beta_{\text{var}}}[\bar{\varphi}] = -\frac{1}{2} \sum_{m=1}^{N} \frac{(m-1)^m}{2N^m} - \frac{2}{\beta_{\text{surf}}}[\bar{\varphi}] \tag{16}$$

$$\frac{2}{\beta_{\text{SAPT}}}[\bar{\varphi}] = -2d_{N+1} + \frac{2}{2N+1} + \frac{1}{2N+1} - \frac{1}{(2N+1)^2} \tag{17}$$

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

$$\lim_{n \to \infty} d_N = \sum_{m=1}^{N} \frac{(m-1)^m}{2N^m} \tag{18}$$

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 $j_0$ coefficients in the asymptotic expansion of $J(R)$ calculated using the multipole expansion of the primitive function $\Phi_N$ 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 $\rho_{N\text{surf}}[\bar{\varphi}], \rho_{N\text{var}}[\bar{\varphi}]$, and $\rho_{N\text{SAPT}}[\bar{\varphi}]$ 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

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