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Generalization of the fourth-order Hylleraas functional for the case of a non-Hermitian unperturbed Hamiltonian

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Generalization of the fourth-order Hylleraas functional form have been performed for the case of non-Hermitian operators. Our new formulas are relevant when the Hermitian Born–Oppenheimer Hamiltonian is decomposed into a non-Hermitian unperturbed part and also a non-Hermitian perturbation. The results can be used to develop BSSE-free intermolecular perturbation theory up to fourth-order.

1. Introduction

Recently, two different but conceptually similar second-order intermolecular perturbation theories have been developed by I. Mayer and us taking into account the "basis set superposition error" (BSSE) according to the *a priori* corrected "chemical Hamiltonian approach" (CHA) [3,7–9]. As it is known, in the CHA scheme we work with non-Hermitian operators because the BSSE is not a physical phenomenon, so no Hermitian operators correspond to it [5]. Additionally, the effective intramolecular Hamiltonian itself is not Hermitian too, due to the basis non-orthogonality. In both perturbation schemes (they are called "CHA-PT2" and "CHA-MP2") the appropriate equations were derived from the form of the second-order Hylleraas functional [2] for the case of a non-Hermitian unperturbed part and also a non-Hermitian perturbation [6]. As these two methods gave results that are in good agrement with the *a posteriori* corrected Boys–Bernardi (BB) ones [1,4], it authorizes us to make an attempt to solve the *a priori* BSSE-free perturbation problem up to fourth-order in the near future. To achieve this, it is very important to obtain an adequate form for the fourth-order Hylleraas functional when the unperturbed Hamiltonian and also the perturbation are not Hermitian. The purpose of the present work is to derive the expression of this required functional.

2. The fourth-order Hylleraas functional for a non-Hermitian unperturbed case

Let us start from the usual Born–Oppenheimer Hamiltonian which is Hermitian, of course. Dividing into two parts this Hamiltonian, where neither $\widehat{H}^0$ nor $\widehat{V}$ are Hermitian, the following equation holds:

$$\widehat{H} = \widehat{H}^0 + \widehat{V} = \widehat{H}^{0\dagger} + \widehat{V}^\dagger = \widehat{H}^\dagger; \tag{1}$$

here the dagger (†) indicates the Hermitian conjugate (or adjoint) of the operator.

Now, we can define the zeroth-order Schrödinger equation as

$$\widehat{H}^0|\mathbf{\Psi}_0\rangle = E_0|\mathbf{\Psi}_0\rangle \quad \text{and} \quad \langle\mathbf{\Psi}_0|\widehat{H}^{0\dagger} = E_0^*\langle\mathbf{\Psi}_0|, \tag{2}$$

where $\mathbf{\Psi}_0$ is the ground-state right eigenvector of $\widehat{H}^0$ and also it is the left eigenvector of $\widehat{H}^{0\dagger}$. We use Dirac's "bra" and "ket" formalism because of the convenience of calculating matrix elements. Since $\widehat{H}^0$ is not Hermitian, we have to permit the possibility of E_0 being complex.

The next step is to define the appropriate form of the wavefunction:

$$|\mathbf{\Psi}\rangle = |\mathbf{\Psi}_0 + \psi_1 + \psi_2 + \psi_3\rangle = |\mathbf{\Psi}_0\rangle + |\psi_1\rangle + |\psi_2\rangle + |\psi_3\rangle, \tag{3}$$

where ψ_1, ψ_2 and ψ_3 are the first-, second- and third-order wavefunctions, respectively.

Consider now the expectation value

$$E = \frac{\langle\mathbf{\Psi}_0 + \psi_1 + \psi_2 + \psi_3|\widehat{H}|\mathbf{\Psi}_0 + \psi_1 + \psi_2 + \psi_3\rangle}{\langle\mathbf{\Psi}_0 + \psi_1 + \psi_2 + \psi_3|\mathbf{\Psi}_0 + \psi_1 + \psi_2 + \psi_3\rangle}. \tag{4}$$

Our aim is to expand this expression up to terms of fourth-order keeping in mind that E is necessarily real. Moreover, we may declare that $\widehat{H}^0$, $\widehat{H}^{0\dagger}$, $|\mathbf{\Psi}_0\rangle$, $\langle\mathbf{\Psi}_0|$, E_0 and E_0^* are zero-order, $\widehat{V}$, $\widehat{V}^\dagger$, $\langle\psi_1|$ and $|\psi_1\rangle$ are first-order, while $\langle\psi_2|$, $|\psi_2\rangle$ and $\langle\psi_3|$, $|\psi_3\rangle$ are second- and third-order quantities, respectively. On the other hand, we do not intend to calculate the explicit form of the higher-order wavefunctions, these results come from an independent CHA calculation (for the first-order see [8]).

To evaluate the expectation value, one may substitute equations (1) and (3) into equation (4):

$$\begin{aligned}
E = \frac{1}{\langle\mathbf{\Psi}_0|\mathbf{\Psi}_0\rangle}\Big[&\langle\mathbf{\Psi}_0|\widehat{H}|\mathbf{\Psi}_0\rangle + E_0\langle\psi_1|\mathbf{\Psi}_0\rangle + \langle\psi_1|\widehat{V}|\mathbf{\Psi}_0\rangle + E_0\langle\psi_2|\mathbf{\Psi}_0\rangle \\
&+ \langle\psi_2|\widehat{V}|\mathbf{\Psi}_0\rangle + E_0\langle\psi_3|\mathbf{\Psi}_0\rangle + \langle\psi_3|\widehat{V}|\mathbf{\Psi}_0\rangle + E_0^*\langle\mathbf{\Psi}_0|\psi_1\rangle + \langle\mathbf{\Psi}_0|\widehat{V}^\dagger|\psi_1\rangle \\
&+ \langle\psi_1|\widehat{H}^0 + \widehat{V}|\psi_1\rangle + \langle\psi_2|\widehat{H}^0 + \widehat{V}|\psi_1\rangle + \langle\psi_3|\widehat{H}^0 + \widehat{V}|\psi_1\rangle + E_0^*\langle\mathbf{\Psi}_0|\psi_2\rangle \\
&+ \langle\mathbf{\Psi}_0|\widehat{V}^\dagger|\psi_2\rangle + \langle\psi_1|\widehat{H}^0 + \widehat{V}|\psi_2\rangle + \langle\psi_2|\widehat{H}^0 + \widehat{V}|\psi_2\rangle + \langle\psi_3|\widehat{H}^0 + \widehat{V}|\psi_2\rangle \\
&+ E_0^*\langle\mathbf{\Psi}_0|\psi_3\rangle + \langle\mathbf{\Psi}_0|\widehat{V}^\dagger|\psi_3\rangle + \langle\psi_1|\widehat{H}^0 + \widehat{V}|\psi_3\rangle + \langle\psi_2|\widehat{H}^0 + \widehat{V}|\psi_3\rangle \\
&+ \langle\psi_3|\widehat{H}^0 + \widehat{V}|\psi_3\rangle\Big]
\end{aligned}$$

$$
\begin{aligned}
&* \left[1 + \frac{\langle\Psi_0|\psi_1\rangle}{\langle\Psi_0|\Psi_0\rangle} + \frac{\langle\Psi_0|\psi_2\rangle}{\langle\Psi_0|\Psi_0\rangle} + \frac{\langle\Psi_0|\psi_3\rangle}{\langle\Psi_0|\Psi_0\rangle} + \frac{\langle\psi_1|\Psi_0\rangle}{\langle\Psi_0|\Psi_0\rangle} + \frac{\langle\psi_1|\psi_1\rangle}{\langle\Psi_0|\Psi_0\rangle}\right.\\
&+ \frac{\langle\psi_1|\psi_2\rangle}{\langle\Psi_0|\Psi_0\rangle} + \frac{\langle\psi_1|\psi_3\rangle}{\langle\Psi_0|\Psi_0\rangle} + \frac{\langle\psi_2|\Psi_0\rangle}{\langle\Psi_0|\Psi_0\rangle} + \frac{\langle\psi_2|\psi_1\rangle}{\langle\Psi_0|\Psi_0\rangle} + \frac{\langle\psi_2|\psi_2\rangle}{\langle\Psi_0|\Psi_0\rangle}\\
&\left.+ \frac{\langle\psi_2|\psi_3\rangle}{\langle\Psi_0|\Psi_0\rangle} + \frac{\langle\psi_3|\Psi_0\rangle}{\langle\Psi_0|\Psi_0\rangle} + \frac{\langle\psi_3|\psi_1\rangle}{\langle\Psi_0|\Psi_0\rangle} + \frac{\langle\psi_3|\psi_2\rangle}{\langle\Psi_0|\Psi_0\rangle} + \frac{\langle\psi_3|\psi_3\rangle}{\langle\Psi_0|\Psi_0\rangle}\right]^{-1}.
\end{aligned}
\tag{5}
$$

Here we used equation (2). It can be seen that several terms are fifth- or higher-order of magnitude and we will omit them in the future considerations. As a consequence of the hermiticity of $\widehat{H}$, the terms where the expectation value of the operators $\widehat{H}^0$ and $\widehat{V}$ or $\widehat{H}^{0\dagger}$ and $\widehat{V}^\dagger$ have been taken between the same wavefunction are automatically real. The only terms which are not guarantied to be real are the fourth-order matrix elements of operators $\widehat{H}^0$ or $\widehat{H}^{0\dagger}$, because the same kind of matrix elements, where the operators $\widehat{H}^0$ or $\widehat{H}^{0\dagger}$ were changed to $\widehat{V}$ or $\widehat{V}^\dagger$, were cancelled, according to that they are *fifth-order* ones. To remove this difficulty, such fourth-order terms will be replaced by their real parts. Considering the expressions of E_0 and E_0^*,

$$
E_0 = \frac{\langle\Psi_0|\widehat{H}^0|\Psi_0\rangle}{\langle\Psi_0|\Psi_0\rangle}, \qquad E_0^* = \frac{\langle\Psi_0|\widehat{H}^{0\dagger}|\Psi_0\rangle}{\langle\Psi_0|\Psi_0\rangle}, \tag{6}
$$

and using the expansion $(1+x)^{-1} = 1 - x + x^2 - x^3 + x^4 - \cdots$, the following formula can be obtained up to fourth-order:

$$
\begin{aligned}
E \approx{}& \frac{1}{\langle\Psi_0|\Psi_0\rangle}\Big[\langle\Psi_0|\widehat{H}|\Psi_0\rangle + E_0\langle\psi_1|\Psi_0\rangle + \langle\psi_1|\widehat{V}|\Psi_0\rangle + E_0\langle\psi_2|\Psi_0\rangle\\
&+ \langle\psi_2|\widehat{V}|\Psi_0\rangle + E_0\langle\psi_3|\Psi_0\rangle + \langle\psi_3|\widehat{V}|\Psi_0\rangle + E_0^*\langle\Psi_0|\psi_1\rangle + \langle\Psi_0|\widehat{V}^\dagger|\psi_1\rangle\\
&+ \langle\psi_1|\widehat{H}^0 + \widehat{V}|\psi_1\rangle + \langle\psi_2|\widehat{H}^0 + \widehat{V}|\psi_1\rangle + \mathrm{Re}\big(\langle\psi_3|\widehat{H}^0|\psi_1\rangle\big)\\
&+ E_0^*\langle\Psi_0|\psi_2\rangle + \langle\Psi_0|\widehat{V}^\dagger|\psi_2\rangle + \langle\psi_1|\widehat{H}^0 + \widehat{V}|\psi_2\rangle + \mathrm{Re}\big(\langle\psi_2|\widehat{H}^0|\psi_2\rangle\big)\\
&+ E_0^*\langle\Psi_0|\psi_3\rangle + \langle\Psi_0|\widehat{V}^\dagger|\psi_3\rangle + \mathrm{Re}\big(\langle\psi_1|\widehat{H}^0|\psi_3\rangle\big)\Big]\\
&* \bigg\{1 - \frac{1}{\langle\Psi_0|\Psi_0\rangle}\Big[\langle\Psi_0|\psi_1\rangle + \langle\Psi_0|\psi_2\rangle + \langle\Psi_0|\psi_3\rangle\\
&+ \langle\psi_1|\Psi_0\rangle + \langle\psi_1|\psi_1\rangle + \langle\psi_1|\psi_2\rangle + \langle\psi_1|\psi_3\rangle + \langle\psi_2|\Psi_0\rangle\\
&+ \langle\psi_2|\psi_1\rangle + \langle\psi_2|\psi_2\rangle + \langle\psi_3|\Psi_0\rangle + \langle\psi_3|\psi_1\rangle\Big]\\
&+ \frac{1}{\langle\Psi_0|\Psi_0\rangle^2}\Big[\big(\langle\Psi_0|\psi_1\rangle + \langle\psi_1|\Psi_0\rangle + \langle\Psi_0|\psi_2\rangle + \langle\psi_2|\Psi_0\rangle + \langle\psi_1|\psi_1\rangle\big)^2\\
&+ 2\big(\langle\Psi_0|\psi_1\rangle + \langle\psi_1|\Psi_0\rangle\big) * \big(\langle\psi_1|\psi_2\rangle + \langle\psi_2|\psi_1\rangle + \langle\Psi_0|\psi_3\rangle + \langle\psi_3|\Psi_0\rangle\big)\Big]\\
&- \frac{1}{\langle\Psi_0|\Psi_0\rangle^3}\Big[\big(\langle\Psi_0|\psi_1\rangle + \langle\psi_1|\Psi_0\rangle\big)^3 + 3\big(\langle\Psi_0|\psi_1\rangle + \langle\psi_1|\Psi_0\rangle\big)^2
\end{aligned}
$$

$$* \big(\langle\psi_1|\psi_1\rangle + \langle\Psi_0|\psi_2\rangle + \langle\psi_2|\Psi_0\rangle\big)\Big] + \frac{1}{\langle\Psi_0|\Psi_0\rangle^4}\big(\langle\Psi_0|\psi_1\rangle + \langle\psi_1|\Psi_0\rangle\big)^4\Big\}. \tag{7}$$

This formula can be rearranged according to the different orders of magnitudes:

$$E \approx \frac{\langle\Psi_0|\widehat{H}|\Psi_0\rangle}{\langle\Psi_0|\Psi_0\rangle} + J_2 + J_3 + J_4, \tag{8}$$

where

$$\begin{aligned} J_2 &= \frac{1}{\langle\Psi_0|\Psi_0\rangle}A, \\ J_3 &= \frac{1}{\langle\Psi_0|\Psi_0\rangle}B - \frac{\langle\Psi_0|\psi_1\rangle + \langle\psi_1|\Psi_0\rangle}{\langle\Psi_0|\Psi_0\rangle^2}A, \\ J_4 &= \frac{1}{\langle\Psi_0|\Psi_0\rangle}C - \frac{\langle\Psi_0|\psi_1\rangle + \langle\psi_1|\Psi_0\rangle}{\langle\Psi_0|\Psi_0\rangle^2}B + \frac{(\Psi_0|\psi_1\rangle + \langle\psi_1|\Psi_0)^2}{\langle\Psi_0|\Psi_0\rangle^2}A \\ &\quad - \frac{(\langle\psi_1|\psi_1\rangle + \langle\Psi_0|\psi_2\rangle + \langle\psi_2|\Psi_0\rangle)}{\langle\Psi_0|\Psi_0\rangle}A \end{aligned} \tag{9}$$

are the second-, third- and fourth-order corrections to the value of the energy. The expressions for A, B and C are

$$\begin{aligned} A &= \langle\psi_1|\widehat{V} - E_1|\Psi_0\rangle + \langle\Psi_0|\widehat{V}^\dagger - E_1^*|\psi_1\rangle + \mathrm{Re}\big(\langle\psi_1|\widehat{H}^0 - E_0|\psi_1\rangle\big), \\ B &= \langle\Psi_0|\widehat{V}^\dagger - E_1^*|\psi_2\rangle + \langle\psi_2|\widehat{V} - E_1|\Psi_0\rangle + \mathrm{Re}\big(\langle\psi_2|\widehat{H}^0 - E_0|\psi_1\rangle\big) \\ &\quad + \mathrm{Re}\big(\langle\psi_1|\widehat{V} - E_1|\psi_1\rangle\big) + \mathrm{Re}\big(\langle\psi_1|\widehat{H}^0 - E_0|\psi_2\rangle\big), \\ C &= \langle\psi_3|\widehat{V} - E_1|\Psi_0\rangle + \langle\Psi_0|\widehat{V}^\dagger - E_1^*|\psi_3\rangle + \mathrm{Re}\big(\langle\psi_2|\widehat{V} - E_1|\psi_1\rangle\big) \\ &\quad + \mathrm{Re}\big(\langle\psi_1|\widehat{V} - E_1|\psi_2\rangle\big) + \mathrm{Re}\big(\langle\psi_3|\widehat{H}^0 - E_0|\psi_1\rangle\big) + \mathrm{Re}\big(\langle\psi_1|\widehat{H}^0 - E_0|\psi_3\rangle\big) \\ &\quad + \mathrm{Re}\big(\langle\psi_2|\widehat{H}^0 - E_0|\psi_2\rangle\big). \end{aligned} \tag{10}$$

Here E_1 and E_1^* are the first-order energy term and its complex conjugate,

$$E_1 = \frac{\langle\Psi_0|\widehat{V}|\Psi_0\rangle}{\langle\Psi_0|\Psi_0\rangle}, \qquad E_1^* = \frac{\langle\Psi_0|\widehat{V}^\dagger|\Psi_0\rangle}{\langle\Psi_0|\Psi_0\rangle}. \tag{11}$$

As it can be seen in equations (10), the formula for J_2 is the same as that obtained by Mayer in [6]. We hope that based on our new result explicit energy expressions can be obtained for the third- and fourth-order BSSE-free intermolecular energy components if one calculates the second- and third-order CHA wavefunctions and substitutes them into the above-derived J_3 and J_4 formulae. Our preliminary numerical results with the second-order CHA-PT2 and CHA-MP2 schemes, which were developed from the expression of J_2 [3,7–9], are very encouraging, completely supporting the present work and the further considerations.

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