Generalization of the Hylleraas functional for calculating BSSE-free intermolecular interactions: further considerations

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The generalized Hylleraas functional necessary for calculating BSSE-free intermolecular interactions is presented for the case when exclusion of BSSE results in non-Hermitian operators and the intra- and intermolecular interactions are treated in different orders of perturbations.

KEY WORDS: Hylleraas functional, perturbation theory, basis set superposition error

1. Introduction

In the recent past, we managed to develop two different but conceptually similar second-order intermolecular perturbation theories which are free from the so-called "basis set superposition error" (BSSE) and based on the *a priori* corrected "chemical Hamiltonian approach" (CHA) [1–5]. These two perturbation methods (they are called "CHA-PT2" and "CHA-MP2") differ only in the orbitals used to construct the unperturbed problem, and both work with non-Hermitian operators because neither the effective intramolecular Hamiltonian nor the perturbation are Hermitian.[1] Therefore, to get the equations to be used in these perturbation theories (PTs) it was first necessary to generalize the usual Hermitian second-order Hylleraas functional form [6] for the case of a non-Hermitian unperturbed part and also a non-Hermitian perturbation [7]. The encouraging numerical results of these PTs usually giving a striking agreement with the *a posteriori* corrected Boys–Bernardi ones [8,9] motivated us to continue this work. Accordingly, in a recent paper we generalized this functional up to fourth-order, in the hope to obtain appropriate equations for a BSSE-free fourth-order intermolecular perturbation theory in the CHA framework [10]. But, after careful considerations we concluded this is very difficult to accomplish. Therefore, it seems to be a reasonable compromise to treat different interactions up to different orders of PT, as it is often done [11,12] in the "symmetry adapted perturbation theory" (SAPT). Namely, we propose to work out

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[1] In the CHA scheme one works with non-Hermitian operators because the BSSE is not a physical phenomenon, so no Hermitian operators correspond to it.

a perturbation scheme in which the intermolecular contributions to the intermolecular interaction energy are calculated up to a higher order of PT than the intramolecular energy components, as only their *changes* contribute to the intermolecular interaction. To achieve this, it is important to obtain the adequate form for such a "mixed-order" (second in intra- and third order in intermolecular interactions) Hylleraas functional when the unperturbed Hamiltonian and also the intra- and intermolecular perturbations are not Hermitian. The purpose of the present work is to derive the expression of the corresponding functional.

In the following section the same technique will be applied as in [10], only the intra- and intermolecular perturbation will be treated separately.

2.   Hylleraas functional based on a non-Hermitian unperturbed Hamiltonian: second order for intra- and third order for intermolecular interactions

Let us consider again the usual Born–Oppenheimer Hamiltonian which is Hermitian, and let us now divide it into three parts, the following equation can be obtained:

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

The dagger (†) denotes the Hermitian conjugate (or adjoint) of the operator. Here $\widehat{H}$, $\widehat{V}$ and $\widehat{W}$ are the unperturbed, the intramolecular and the intermolecular Hamiltonians, respectively, and they are not Hermitian separately, only their sum is Hermitian.

The zeroth-order Schrödinger equation is

$$\widehat{H}^0|\Psi_0\rangle = E_0|\Psi_0\rangle \quad \text{and} \quad \langle\Psi_0|\widehat{H}^{0\dagger} = E_0^*\langle\Psi_0|, \tag{2}$$

where Ψ_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 allow the possibility of E_0 being complex.

Now, the following step is to introduce an appropriate form of the wavefunction:

$$|\Psi\rangle = |\Psi_0 + \psi_1 + \psi_2 + \psi_3\rangle = |\Psi_0\rangle + |\psi_1\rangle + |\psi_2\rangle + |\psi_3\rangle, \tag{3}$$

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

But, differently from our earlier cases [10], we need to continue further the partition of the higher-order parts of the wavefunctions by introducing different order parameters for the terms corresponding to the intra- and intermolecular effects:

$$\psi_1 = \psi_1^{10} + \psi_1^{01}, \quad \psi_2 = \psi_2^{11} + \psi_2^{02}, \quad \psi_3 = \psi_3^{12}. \tag{4}$$

In our notations the subscripts show the *overall* order of the given wavefunction component, while the superscripts indicate how the orders are distributed between intra- and intermolecular interactions. As noted above, we are less interested in intramolecular effects than in the intermolecular ones; accordingly, terms ψ_2^{20} and ψ_3^{21} are absent in the

above expressions.[2] Generally, we keep the terms up to the second order in the intra-molecular and third order in the intermolecular interactions. We start again from the same expectation value as in [10],

$$E = \frac{\langle \Psi_0 + \psi_1 + \psi_2 + \psi_3 | \widehat{H} | \Psi_0 + \psi_1 + \psi_2 + \psi_3 \rangle}{\langle \Psi_0 + \psi_1 + \psi_2 + \psi_3 | \Psi_0 + \psi_1 + \psi_2 + \psi_3 \rangle}. \tag{5}$$

Let us expand this expression up to terms of orders indicated above, and keep in mind that E is necessarily real. In addition, we may state that $\widehat{H}^0$, $\widehat{H}^{0\dagger}$, $|\Psi_0\rangle$, $\langle\Psi_0|$, E_0 and E_0^* are zero-order, $\widehat{V}$, $\widehat{V}^\dagger$, $\widehat{W}$, $\widehat{W}^\dagger$ $\langle\psi_1|$ 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.

Similarly to our earlier work [10], we also do not intend to calculate here the actual form of the higher-order wavefunctions, the explicit results should come from an independent CHA calculation (for the first order see [2]).

To consider the above-defined expectation value, one needs to substitute equations (1) and (3) into equation (5):

$$\begin{aligned}
E = \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}+\widehat{W}|\Psi_0\rangle + E_0\langle\psi_2|\Psi_0\rangle \\
&+ \langle\psi_2|\widehat{V}+\widehat{W}|\Psi_0\rangle + E_0\langle\psi_3|\Psi_0\rangle + \langle\psi_3|\widehat{V}+\widehat{W}|\Psi_0\rangle + E_0^*\langle\Psi_0|\psi_1\rangle \\
&+ \langle\Psi_0|\big(\widehat{V}+\widehat{W}\big)^\dagger|\psi_1\rangle + \langle\psi_1|\widehat{H}^0+\widehat{V}+\widehat{W}|\psi_1\rangle + \langle\psi_2|\widehat{H}^0+\widehat{V}+\widehat{W}|\psi_1\rangle \\
&+ \langle\psi_3|\widehat{H}^0+\widehat{V}+\widehat{W}|\psi_1\rangle + E_0^*\langle\Psi_0|\psi_2\rangle + \langle\Psi_0|\big(\widehat{V}+\widehat{W}\big)^\dagger|\psi_2\rangle \\
&+ \langle\psi_1|\widehat{H}^0+\widehat{V}+\widehat{W}|\psi_2\rangle + \langle\psi_2|\widehat{H}^0+\widehat{V}+\widehat{W}|\psi_2\rangle + \langle\psi_3|\widehat{H}^0+\widehat{V}+\widehat{W}|\psi_2\rangle \\
&+ E_0^*\langle\Psi_0|\psi_3\rangle + \langle\Psi_0|\big(\widehat{V}+\widehat{W}\big)^\dagger|\psi_3\rangle + \langle\psi_1|\widehat{H}^0+\widehat{V}+\widehat{W}|\psi_3\rangle \\
&+ \langle\psi_2|\widehat{H}^0+\widehat{V}+\widehat{W}|\psi_3\rangle + \langle\psi_3|\widehat{H}^0+\widehat{V}+\widehat{W}|\psi_3\rangle \Big] \\
\times \Big[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} \\
&+ \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} \\
&+ \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} \Big]^{-1}.
\end{aligned} \tag{6}$$

Here we used equation (2), and no simplifications have been as yet introduced. However, it can be found that several terms are of the fourth or higher order and we will neglect them in the following. As a consequence of the Hermiticity of $\widehat{H}$ the terms where the expectation value of the operators $\widehat{H}^0$, $\widehat{V}$ and $\widehat{W}$ or $\widehat{H}^{0\dagger}$, $\widehat{V}^\dagger$ and $\widehat{W}^\dagger$ have been taken with the same function in the "bra" and "ket" are automatically real. However, there are

[2] For example, ψ_2 is a second-order quantity which can be written as a sum of ψ_2^{11} (containing first-order excitations both in the intra- and the intermolecular pieces) and ψ_2^{02} (where only the intermolecular part contains second-order excitations, while the intramolecular one is in the ground state).

terms which are not obviously real. In order to get a real energy, a special care should be taken by expanding the total Hermitian Hamiltonian either as $\widehat{H} = \widehat{H}^0 + \widehat{V} + \widehat{W}$ or as $\widehat{H} = \widehat{H}^\dagger = \widehat{H}^{0\dagger} + \widehat{V}^\dagger + \widehat{W}^\dagger$ similarly to the technique used in [5,10]. A special care was necessary to some terms which are unsymmetric in respect of interchanging $\widehat{V}$ and $\widehat{W}$, as we treat intra- and intermolecular interactions on a different footing.

These difficulties can be solved by collecting the terms which resulting the real parts of the different contributions. Considering the expressions of E_0 and E_0^*:

$$E_0 = \frac{\langle \Psi_0 | \widehat{H}^0 | \Psi_0 \rangle}{\langle \Psi_0 | \Psi_0 \rangle}, \quad E_0^* = \frac{\langle \Psi_0 | \widehat{H}^{0\dagger} | \Psi_0 \rangle}{\langle \Psi_0 | \Psi_0 \rangle}, \tag{7}$$

and using the expansion $(1 + x)^{-1} = 1 - x + x^2 - x^3 + x^4 - \cdots$, the following formula can be obtained up to the third 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 + \langle \psi_1 | \widehat{W} | \Psi_0 \rangle \\
& + E_0 \langle \psi_2 | \Psi_0 \rangle + \langle \psi_2 | \widehat{V} | \Psi_0 \rangle + \langle \psi_2 | \widehat{W} | \Psi_0 \rangle + E_0 \langle \psi_3 | \Psi_0 \rangle + E_0^* \langle \Psi_0 | \psi_1 \rangle \\
& + \langle \Psi_0 | \widehat{V}^\dagger | \psi_1 \rangle + \langle \Psi_0 | \widehat{W}^\dagger | \psi_1 \rangle + \langle \psi_1 | \widehat{H}^0 + \widehat{V} + \widehat{W} | \psi_1 \rangle - \langle \psi_1^{10} | \widehat{V} | \psi_1^{10} \rangle \\
& + \mathrm{Re}\big(\langle \psi_2 | \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_0 | \widehat{W}^\dagger | \psi_2 \rangle \\
& + \mathrm{Re}\big(\langle \psi_1 | \widehat{H}^0 | \psi_2 \rangle \big) + E_0^* \langle \Psi_0 | \psi_3 \rangle \Big] \\
& \times \Big\{ 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_2 | \Psi_0 \rangle + \langle \psi_2 | \psi_1 \rangle + \langle \psi_3 | \Psi_0 \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 \big) \big(\langle \Psi_0 | \psi_1 \rangle + \langle \Psi_0 | \psi_2 \rangle \\
& + \langle \psi_1 | \Psi_0 \rangle + \langle \psi_2 | \Psi_0 \rangle + \langle \psi_1 | \psi_1 \rangle \big) \\
& + \big(\langle \Psi_0 | \psi_2 \rangle + \langle \psi_2 | \Psi_0 \rangle + \langle \psi_1 | \psi_1 \rangle \big) \big(\langle \Psi_0 | \psi_1 \rangle + \langle \psi_1 | \Psi_0 \rangle \big) \big] \\
& - \frac{1}{\langle \Psi_0 | \Psi_0 \rangle^3} \big(\langle \Psi_0 | \psi_1 \rangle + \langle \psi_1 | \Psi_0 \rangle \big)^3 \Big\}.
\end{aligned} \tag{8}$$

This formula can be rearranged according to the different orders:

$$E \approx \frac{\langle \Psi_0 | \widehat{H} | \Psi_0 \rangle}{\langle \Psi_0 | \Psi_0 \rangle} + J_2 + J_3, \tag{9}$$

where

$$\begin{aligned}
J_2 &= \frac{1}{\langle \Psi_0 | \Psi_0 \rangle} A, \\
J_3 &= \frac{1}{\langle \Psi_0 | \Psi_0 \rangle} B - \frac{\langle \Psi_0 | \psi_1 \rangle + \langle \psi_1 | \Psi_0 \rangle}{\langle \Psi_0 | \Psi_0 \rangle^2} A + \frac{\langle \Psi_0 | \psi_1^{10} \rangle + \langle \psi_1^{10} | \Psi_0 \rangle}{\langle \Psi_0 | \Psi_0 \rangle^2} A'
\end{aligned} \tag{10}$$

are the second- and third-order corrections to the value of the energy. The J_3 contains only intermolecular correction to the interaction energy.

The expressions for A, A' and B are:

$$A = \langle \psi_1 | \widehat{V} + \widehat{W} - E_1 | \Psi_0 \rangle + \langle \Psi_0 | (\widehat{V} + \widehat{W})^\dagger - E_1^* | \psi_1 \rangle + \mathrm{Re}(\langle \psi_1 | \widehat{H}^0 - E_0 | \psi_1 \rangle),$$

$$A' = \langle \psi_1^{10} | \widehat{V} - E_1^{\mathrm{intra}} | \Psi_0 \rangle + \langle \Psi_0 | \widehat{V}^\dagger - E_1^{\mathrm{intra}*} | \psi_1^{10} \rangle + \mathrm{Re}(\langle \psi_1^{10} | \widehat{H}^0 - E_0 | \psi_1^{10} \rangle),$$

$$B = \langle \Psi_0 | (\widehat{V} + \widehat{W})^\dagger - E_1^* | \psi_2 \rangle + \langle \psi_2 | \widehat{V} + \widehat{W} - E_1 | \Psi_0 \rangle + \mathrm{Re}(\langle \psi_2 | \widehat{H}^0 - E_0 | \psi_1 \rangle) \quad (11)$$
$$+ \mathrm{Re}(\langle \psi_1 | \widehat{V} + \widehat{W} - E_1 | \psi_1 \rangle) - \mathrm{Re}(\langle \psi_1^{10} | \widehat{V} - E_1^{\mathrm{intra}} | \psi_1^{10} \rangle)$$
$$+ \mathrm{Re}(\langle \psi_1 | \widehat{H}^0 - E_0 | \psi_2 \rangle).$$

Here E_1 and E_1^* are the total (intra + inter) first-order energy term and its complex conjugate:

$$E_1 = \frac{\langle \Psi_0 | \widehat{V} + \widehat{W} | \Psi_0 \rangle}{\langle \Psi_0 | \Psi_0 \rangle}, \quad E_1^* = \frac{\langle \Psi_0 | (\widehat{V} + \widehat{W})^\dagger | \Psi_0 \rangle}{\langle \Psi_0 | \Psi_0 \rangle}, \quad (12)$$

while E_1^{intra} and $E_1^{\mathrm{intra}*}$ are the first-order pure intramolecular energy and its complex conjugate:

$$E_1^{\mathrm{intra}} = \frac{\langle \Psi_0 | \widehat{V} | \Psi_0 \rangle}{\langle \Psi_0 | \Psi_0 \rangle}, \quad E_1^{\mathrm{intra}*} = \frac{\langle \Psi_0 | (\widehat{V})^\dagger | \Psi_0 \rangle}{\langle \Psi_0 | \Psi_0 \rangle}. \quad (13)$$

As it can be seen in equation (10), the formula for J_2 is the same as that obtained in [7,10]. It is interesting to note that both the second and third terms of equation (10) contain third-order intramolecular contributions, but they exactly cancel, so the resulting theory is only second-order in the intramolecular interactions – as it was intended. We expect that the inclusion of a second-order interaction term in the PT permits taking into account properly those polarization and charge transfer effects which were lacking from our CHA-PT2 theory.

Acknowledgements

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