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Padé-resummed fourth-order many-body perturbation theory: Applications to the description of Au–Au, Au–Hg, and Hg–Hg bonds

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ABSTRACT

Pilot applications of Padé-resummed fourth-order many-body perturbation theory to the description of chemical bonds with strong contributions from the interactions of filled *d*-shells (Au–Au, Au–Hg, and Hg–Hg) are reported. The employed Padé approximants, especially the constrained [0/1,1] quadratic one, ensure radical improvements of accuracy with respect to the partial summation. The non-separability problem is discussed and bypassed through the direct resummation of perturbative expansions for differential correlation energies.

1. Introduction

Fourth-order Møller–Plesset many-body perturbation theory, MBPT(4), is a valuable tool for ab initio correlation calculations on ground electronic states of molecular systems, widely used both as is and as a part of composite computational schemes. The main advantages of this technique consist in conceptual transparency, exact size-consistency (and even separability) of energy estimates, and particular suitability for efficient parallel computer implementation. In many situations admitting the single-reference representation of wavefunctions, MBPT(4) offers a possibility to achieve a reasonable accuracy with moderate computational efforts, especially for light-element compounds. However, the domination of a single determinant in the expansion of a wavefunction does not guarantee a rapid and regular convergency of MBPT series and thus the reliability of fourth-order energy estimates. Particularly severe problems appear for the systems composed of heavy 11 and 12 group elements with strongly interacting filled *d*-shells, where the correlation contributions to bond energies are comparable to these energies themselves (see, e.g. [1,2]).

To improve the accuracy of finite-order MBPT calculations, various extrapolation techniques have been developed and extensively tested in the calculations on light-element compounds [3–7, and references cited therein]. Although the utility of such techniques is incontestable, none of them seems to be universally efficient, so that the results of their applications to the compounds of heavy group 11 and 12 metals are hardly predictable. Taking into account the particular practical importance of rather complex systems composed of these elements (e.g. those comprising Au clusters) and the difficulties in their description by popular low-order MBPT and DFT-based methods [1,2,8], it is of interest to study the performance of MBPT(4) with subsequent extrapolation as a tool of potential energy surface calculations for such systems.

In contradistinction with the case of light-element compounds, one can hardly make use of full configuration interaction (FCI) benchmark calculations even for the simplest molecules composed of heavy transition metals, since a qualitatively correct description of bonding in these systems requires to correlate a large number of electrons and to discretize the Hamiltonians with extensive basis sets. To estimate the accuracy of approximate schemes, one can try to reproduce the results of coupled cluster calculations with fully optimized single, double and triple amplitudes (CCSDT) within the same one-electron basis; alternatively, experimental data can be employed as a reference. In the latter case, the use of large bases (and the extrapolation to the complete basis set limit) as well as a proper account of relativistic effects are compulsory.

Additional difficulties in assessing the performance and practical use of conventional extrapolation schemes stems from the lack of separability of resulting correlation energy estimates. As is shown below, this feature can lead to catastrophic errors in studies on large heterogeneous systems. To rely on the results of tests performed with small molecules, one has to restore the separability, at least to a certain extent.

In this Letter, I present and analyze the results of MBPT(4) calculations followed by the resummation by means of conventional (rational) and quadratic Padé approximants (PA) for the Au–Au, Au–Hg, and Hg–Hg bonds in diatomic molecules. In Section 2, the employed extrapolation schemes are specified and the non-separability problem is discussed. Section 3 provides the details

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of the computations. In the next section, the accuracy of MBPT(4)/PA parameters of chemical bonds is estimated via the comparison with those obtained from CCSDT calculations and available experimental data. Section 5 contains some concluding remarks.

2. Preliminary remarks

Consider the conventional Møller–Plesset MBPT series for the total energy E of a many-electron system [9],

$$E(z) = \sum_{n=0}^{\infty} e_n z^n, \tag{1}$$

where z is the perturbation parameter; the Nth partial sum of this series will be denoted by $E^{[N]}(z)$. The physical solution corresponds to $z = 1$; $E(1)$ is the (lowest) eigenvalue of the true many-electron Hamiltonian, $E^{[1]}(1) = e_0 + e_1 = E_{\mathrm{HF}}$ is the Hartree–Fock energy and the subsequent partial sums, $E^{[N]}(1)$, are the MBPT(N) energies.

To estimate the sum of the series (1) known up to the Nth order, one widely uses *rational Padé approximants* $[L/M](z) = A_L(z)/B_M(z)$, composed of two polynomials $A_L(z)$ and $B_M(z)$ of degrees L and M, respectively ($L + M = N$) and having the same expansion in powers of z as $E(z)$ up to the Nth order.

Since the separation of E_{HF} into e_0 and e_1 and the choice of the zero of the energy scale are quite arbitrary, it is highly desirable to avoid the dependence of approximants on these two factors. This is readily achieved for even-order MBPT by using the $[L/L-1]$ PAs which are invariant with respect to the shift of the zero-order spectrum and the origin of energy scale (see [3,7, and references cited therein]). Unfortunately, none of non-trivial rational approximant with $L + M = 4$ shares this property. To solve this problem, it is convenient to rewrite the series (1) as

$$E(z) = e_0 + e_1 z + \delta E(z) z^2, \quad \delta E(z) = e_2 + e_3 z + e_4 z^2 + \cdots, \tag{2}$$

and to construct an approximant for $\delta E(z)$ rather than for $E(z)$ [4,10]; obviously, $\delta E(1)$ is the correlation energy.

Two rational approximants for δE ensuring reasonable asymptotic behavior of $E(z)$ for large perturbation parameter values are used in the present work:

Unconstrained [0/2] PA. One readily verifies that it yields exactly the same correlation energy estimates as the [2/2] approximant for $E(z)$ derived from the series (1) with the choice of zero-order Hamiltonian and the origin of the energy scale defined by the condition $e_0 = e_1 = 0$,

[1/2] PA with the constraint corresponding to an intuitive 'geometrical' estimate for e_5: $e_5 = e_3 \cdot e_4/e_2$. This approximant which will be denoted by $[1/2]_n$ is somewhat trivial because $[1/2]_n$ for $z = 1$ coincides with the sum of two geometrical series (for odd and even orders) with the same common ratio e_4/e_2 which has been used to estimate the sums of MBPT series in [11,12]. It is also equivalent to the $[3/2]_n$ approximant for the total energy introduced in Ref. [8].

Alternatively, one can fit $\delta E(z)$ by a *quadratic Padé approximant* $[L/M,K]$

$$[L/M,K](z) = \frac{1}{2B_M(z)}\left(A_L(z) \pm \sqrt{A_L(z)^2 - 4B_M(z)C_K(z)}\right), \tag{3}$$

build of three polynomials, $A_L(z)$, $B_M(z)$, and $C_K(z)$ (the subscripts still indicate the degrees of polynomials). It is believed (see [7,13, and references cited therein]) that the essential advantage of quadratic Padé approximants consists in their capability to model square-root branch point singularities of $E(z)$. The branch point positions are determined by the condition $A_L(z)^2 - 4B_M(z)C_K(z) = 0$.

There are quite a few variants of non-trivial quadratic Padé approximants for $\delta E(z)$ which can be constructed from the results of fourth-order calculations; furthermore, it is desirable to avoid high powers of z in the asymptotical expression for $E(z)$. Here I employ the unconstrained [0/1,0] approximant and the [0/1,1] one constrained by the condition $C_1(0) = 0$ [6]. The former function has a single branch point located on the real axis, while the latter one can have two different real branch points or a conjugated pair of complex branch points, depending on the behavior of the series.

The presence of branch points in the vicinity of the origin ($z = 0$) can seriously affect the accuracy of quadratic Padé approximation. Goodson [14] proposed to regularize the perturbation expansion (1) by an appropriate Feenberg-like rearrangement [15] $\{e_n\} \to \{e'_n\}$

$$e'_n(\lambda) = \frac{1}{(1-\lambda)^{n-1}} \sum_{j=2}^{n} \binom{n-2}{j-2} (-\lambda)^{n-j} e_j, \quad n \geqslant 2, \tag{4}$$

choosing the transformation parameter λ to push the dangerous branch points of quadratic PA from the origin. I shall consider only the case of [0/1,1] approximants and choose λ by maximizing the distance of branch point in the negative half-plane from the origin (the optimal parameter value and the corresponding approximant will be denoted by λ_r and $[0/1,1]_r$) or from the imaginary axis (λ_z and $[0/1,1]_z$).

One readily verifies that all rational and quadratic PA listed above are extensive, i.e. the approximant for the correlation energy of a system composed of identical non-interacting subsystem coincides with the sum of corresponding approximants for subsystem correlation energies. However, none of them is separable; if the coefficients of perturbation expansions for the correlation energies of two non-interacting subsystems A and B (δE^A and δE^B) are not proportional, the Padé approximant for the overall correlation energy $\delta\widetilde{E}^{AB}$ differs from the sum of the corresponding approximants for the correlation energies of the subsystems $\left(\delta\widetilde{E}^A + \delta\widetilde{E}^B\right)$. Practical consequences of this fact can be disastrous. Suppose that $|\delta E^A| \gg |\delta E^B|$ and note that for $z = 1$ each approximant $\delta\widetilde{E}$ can be represented in the form

$$\delta\widetilde{E} = e_2 f(e_3/e_2, e_4/e_2),$$

where f depends only on the ratios of perturbative corrections. Taking into account the separability of finite-order energy corrections, one can conclude that

$$e_n^{AB}/e_2^{AB} \approx e_n^A/e_2^A, \quad n = 3,4,$$

and

$$\delta\widetilde{E}^{AB} \approx \left(e_2^A + e_2^B\right) f\left(e_3^A/e_2^A, e_4^A/e_2^A\right) = \delta\widetilde{E}^A + e_2^B f\left(e_3^A/e_2^A, e_4^A/e_2^A\right). \tag{5}$$

The last term in (5) should provide an estimate for the correlation energy of the subsystem B, but its deviation from the second-order value e_2^B is fully determined by the properties of the subsystem A. One can imagine, for instance, the impact of such unphysical behavior of approximants on the calculated properties of an atom or a small molecule, weakly adsorbed on a relatively large cluster.

The mentioned problem can be bypassed through constructing the approximants for *differential correlation energies* associated with some processes (e.g. deformations of nuclear configurations, fragmentation of a molecule, ionization or electron attachment, etc.) rather than for total correlation energies, i.e. by resumming the power series obtained as the difference of two conventional MBPT expansions. In this case, the perturbative contributions associated with any inert (separated) subsystem vanish and cannot affect the analog of $f(e_3/e_2, e_4/e_2)$. One should realize that the proposed solution is far from perfection, at least because the results become dependent on the choice of the reference point (e.g. start-