

The size-extensivity of correlation energy estimators based on effective characteristic polynomials

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Abstract

Estimators Π_n for the correlation energy can be computed as roots of effective characteristic polynomials of degree n . The coefficients of these polynomials are derived from the terms of the perturbation series of the energy. From a fourth-order Møller–Plesset (MP4) calculation one can calculate with negligible effort a size-extensive estimator Π_2 that is in many cases much closer to the full CI correlation energy of the ground state than the MP4 value [H.H.H. Homeier, *J. Mol. Struct. (Theochem)*, 366 (1996) 161]. Here, we prove that the estimators Π_n for $n > 2$ are size-extensive if they are calculated from the MP series. © 1997 Elsevier Science B.V.

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1. Introduction

Many-body perturbation theory is a convenient tool to estimate the correlation energy of molecular systems. Usually, one calculates an estimate for the correlation energy by term-by-term summation of the Møller–Plesset (MP) series

$$E = E_0 + E_1 + E_2 + E_3 + E_4 + E_5 + \dots \quad (1)$$

as a partial sum

$$E^{(n)} = \sum_{j=0}^n E_j \quad (2)$$

that is usually denoted by MP_n . But this approximate value does not optimally exploit the information content of the terms E_j of the MP series. Better estimates

can be obtained by using convergence acceleration or extrapolation methods to sum the perturbation series, as for instance Padé approximants or methods based on effective characteristic polynomials. The method of effective characteristic polynomials has been introduced by Čížek and co-workers recently. It has been applied to the summation of the divergent perturbation series of anharmonic oscillators [1] and to correlation energies of model systems [2–8]. Extensions of the method for the simultaneous treatment of several perturbation series have recently been proposed [9] but this will not be considered in the following.

If only perturbation energies up to the fourth order are available then one can use the Π_2 estimator [10]. The Π_2 estimator is obtained as a root of a second-degree effective characteristic polynomial. The coefficients of this polynomial are related to the terms of the perturbation series. The Π_2 estimator can be calculated easily from the terms E_0, \dots, E_4 of the MP

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series and is size-extensive. As is well known, the latter property is important for the treatment of larger systems. For a series of benchmark systems the Π_2 estimator proved to be relatively accurate compared with a number of other estimators [10].

Analogous estimators Π_n can be derived from effective characteristic polynomials of higher degrees n . In the present contribution, we sketch the method of effective characteristic polynomials, basically to fix notation. Then, it is proved that the estimators Π_n for $n > 2$ are also size-extensive if the underlying perturbation theory is size-extensive, as is the case for the MP series.

2. Correlation energy estimators based on effective characteristic polynomials

In this section, we sketch the method of the effective characteristic polynomials. The characteristic polynomial $P_n(E)$ of degree n in the unknown energy E has in the linear variation method the form

$$P_n(E) = \det \langle \phi_j | H | \phi_k \rangle - E \delta_{j,k} \quad (3)$$

where $\{\phi_j\}_{j=1}^n$ are n orthonormal basis functions, and H is the Hamiltonian. If the Hamiltonian can be written as $H = H_0 + \beta V$, the polynomial has the form ([1], Eq. (3.2))

$$P_n(E) = \sum_{j=0}^n E^j \sum_{k=0}^{n-j} f_{n,j,k} \beta^k \quad (4)$$

with $f_{n,n,0} = 1$. This leaves $L + 1$ coefficients $f_{n,j,k}$ to be determined where $L = n(n + 3)/2 - 1$. In the method of the characteristic polynomial, they are obtained from the coefficients E_j of the perturbation series for E

$$E = \sum_{j=0}^{\infty} E_j \beta^j \quad (5)$$

Since $P_n(E) = 0$ for an eigenvalue E , one demands

$$P_n(E_0 + \beta E_1 + \beta^2 E_2 + \dots) = O(\beta^{L+1}) \quad (6)$$

This means that the first $L + 1$ coefficients of the Taylor series (in β) of the left-hand side of this equation, i.e., up to the coefficient of β^L , all have to vanish. This yields a linear equation system for the unknown $f_{n,j,k}$. We assume in the following that this linear equation system yields a unique solution for the coefficients $f_{n,j,k}$. After the determination of the coefficients, the effective characteristic polynomial is fixed and also

denoted by $P_n(E) = P_n[E_0, \dots, E_L](E)$ in order to make the dependence on the terms E_j explicit. The effective characteristic equation $P_n[E_0, \dots, E_L](E) = 0$ may then be solved for E . The lowest root is called $\Pi_n[E_0, \dots, E_L]$ or, more simply, Π_n , if the values of the E_j are plain from the context.

In the case $n = 2$ one obtains for $\beta = 1$ the simple expression

$$\Pi_2 = E_0 + E_1 + \frac{E_2^2}{2} \frac{E_2 - E_3}{E_2 E_4 - E_3^2} - \frac{E_2^2}{2} \left[\frac{(E_2 - E_3)^2 - 4(E_2 E_4 - E_3^2)}{(E_2 E_4 - E_3^2)^2} \right]^{1/2} \quad (7)$$

3. Proof of the size-extensivity

Consider a supersystem composed of M identical, non-interacting subsystems. Then, the true energy of the supersystem is the M -fold of the energy of a single subsystem. An approximate method for the computation of the energy is called size-extensive if the approximate energy for the supersystem is the M -fold of the approximate energy of a single subsystem.

It is well known that MP perturbation theory is size-extensive order by order. This means that for all $k \geq 0$ the k th order term of the perturbation series for the supersystem equals $M E_k$ if the k th order term of the perturbation series of a single subsystem is E_k . This implies that the MP k estimator is size-extensive for each order k .

In order to prove size-extensivity of the Π_n estimators with $n > 2$, one thus has to show that for each n and M the equation

$$\Pi_n[M E_0, \dots, M E_L] = M \Pi_n[E_0, \dots, E_L] \quad (8)$$

holds where, as before, $L = n(n + 3)/2 - 1$.

For given M and n and for given E_0, \dots, E_L and β , we can consider the $f_{n,j,k}$ and hence, also the effective characteristic polynomial

$$P_n[E_0, \dots, E_L](E) = \sum_{j=0}^n E^j \sum_{k=0}^{n-j} f_{n,j,k} \beta^k \quad (9)$$

as known. We introduce a new polynomial by

$$\tilde{P}_n(E) = M^n P_n[E_0, \dots, E_L](E/M) \quad (10)$$

$$= \sum_{j=0}^n E^j \sum_{k=0}^{n-j} [f_{n,j,k} M^{n-j}] \beta^k \quad (11)$$

Eq. (10) defines the polynomial, while Eq. (11) shows that $\tilde{P}_n(E)$ can also be regarded as an effective characteristic polynomial with new coefficients $\tilde{f}_{n,j,k} = f_{n,j,k}M^{n-j}$. Note that $\tilde{f}_{n,n,0} = 1$ holds as required.

Since

$$\begin{aligned} &\tilde{P}(ME_0 + \beta ME_1 + \beta^2 ME_2 + \dots) \\ &= M^n P_n[E_0, \dots, E_L](E_0 + \beta E_1 + \beta^2 E_2 + \dots) = O(\beta^{L+1}) \end{aligned} \quad (12)$$

the polynomial $\tilde{P}_n(E)$ is identical to the effective characteristic polynomial for the energies ME_0, \dots, ME_L , i.e.

$$M^n P_n[E_0, \dots, E_L](E/M) = P_n[ME_0, \dots, ME_L](E) \quad (13)$$

Thus, the complete pattern of roots is scaled by M , since if ϵ is any root of $P_n[E_0, \dots, E_L](E)$ then $M\epsilon$ is a root of $P_n[ME_0, \dots, ME_L](E)$. But this proves Eq. (8) since $\Pi n[E_0, \dots, E_L]$ is a root of $P_n[E_0, \dots, E_L](E)$.

4. Concluding remarks

Size-extensivity is an important property that is helpful for obtaining reliable energy estimates for larger systems. It is hoped that correlation energy estimates on the basis of effective characteristic polynomials will become more widespread since they offer a conceptually and computationally relatively simple but accurate computational tool as demonstrated in [10]. Only the MP series has to be computed, and its terms be combined to obtain an effective characteristic polynomial and the correlation energy as one of its roots as in Eq. (7). Some error control is possible by comparison with some other methods for convergence acceleration of the perturbation series [10].

An extension of the method was proposed by the author in [9]. It allows us to combine information from the terms of several short perturbation expansions for a small number of states. These simultaneous perturbation series can also be used for the construction of a characteristic polynomial. In this way, the somewhat demanding relationship between the degree of the characteristic polynomial and the maximum order of the perturbation calculation is largely avoided. Applications of this extended method and a proof of its size-extensivity are currently under investigation.

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