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Connected-Moments Expansion: A New Tool for Quantum Many-Body Theory

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The connected-moments expansion (CMX) for the ground-state energy is derived from the Horn-Weinstein theorem. This new technique possesses several striking advantages over traditional approaches to calculation of the ground-state energy. Like perturbational theories, the CMX series is conceptually simple but is easier to derive and program and is usually convergent even for very "crude" trial kets. Numerical examples reveal potential applicability of CMX for calculation of the correlation energy when the trial ket has the form of a multideterminant wave function.

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A very interesting theorem concerning the ground-state energy of the many-body systems has been formulated recently by Horn and Weinstein.[1] Let $|\phi\rangle$ be a normalized trial ket which has a nonzero overlap with the exact ground-state wave function of the system under consideration. Then the function

$$F(t)=\langle\phi|\exp(-t\hat{H})\hat{H}|\phi\rangle/\langle\phi|\exp(-t\hat{H})|\phi\rangle$$
$$=\sum_{k=0}^{\infty}(-t)^k I_{k+1}/k! \qquad (1)$$

converges to the *exact* ground-state energy E_0 at the limit $t\rightarrow\infty$. The coefficients I_k are connected moments of the Hamiltonian:

$$I_k=\langle H^k\rangle-\sum_{i=0}^{k-2}\binom{k-1}{i}I_{i+1}\langle H^{k-i-1}\rangle; \qquad (2)$$
$$\langle H^k\rangle=\langle\phi|\hat{H}^k|\phi\rangle.$$

The theorem, although having some importance for quantum mechanics, cannot be simply utilized for any practical calculations. In order to calculate the limit $F(\infty)$, one has to know all the connected moments, which is not feasible for any real system. Horn and Weinstein used Padé approximants to obtain some practical procedures for the estimation of ground-state energy, but their approach appears to be not general enough to be treated as a universal tool for the quantum-mechanical calculations.

In our communication we present a connected-moments expansion (CMX) technique that benefits from the validity of the Horn-Weinstein theorem and, on the other hand, is simple and general. Let us recall general properties of the function $F(t)$.[1] $F(t)$ is a monotonically decreasing function of t and $F(0)=\langle\phi|\hat{H}|\phi\rangle$. Moreover, for a system of N independent particles, $F(t)$ scales linearly with N for any value of t. From this we conclude easily that the coefficients I_k also scale linearly with N. In other words, both $F(t)$ and the I_k's are size-extensive.[2] The above properties convince us to express $F(t)$ as

$$F(t)=E_0+\sum_{j=1}^{\infty}A_j\exp(-b_jt);\quad b_j>0. \qquad (3)$$

The coefficients A_j and b_j can be found by a direct comparison of Eq. (1) with the Taylor expansion of the exponential terms in Eq. (3). This defines the coefficients P_k as

$$P_1=I_1-E_0=\sum_{j=0}^{\infty}A_j; \qquad (4a)$$

$$P_k=I_k=\sum_{j=0}^{\infty}A_jb_j^{k-1},\quad k>1. \qquad (4b)$$

Since the A_j's and b_j's depend solely on the coefficients

P_k $(k>1)$, the quantity P_1 can be expressed as some function of them. This means that the ground-state energy E_0 can be expressed as a function of the I_k's. Let us suppose that we are able to approximate P_1 by a sum of W_k in the expansion

$$P_1 = \sum_{k=1}^{\infty} W_k(P_2, P_3, \dots). \tag{5}$$

Our problem is to find out the explicit form of the W_k's. In order to accomplish that, we study the quantities

$$\begin{aligned} S_k &= P_k P_{k+2} - P_{k+1}^2 \\ &= \sum_{i,j=1}^{\infty} A_i A_j (b_j^2 - b_i b_j)(b_i b_j)^{k-1}. \end{aligned} \tag{6}$$

Inspection of formulas (4) and (6) reveals that they are completely analogous, except that in Eq. (6) A_i is replaced by $A_i A_j (b_j^2 - b_i b_j)$ and b_i by $b_i b_j$. Therefore, the S_k's must also conform to the formula (5):

$$S_1 = \sum_{k=1}^{\infty} W_k(S_2, S_3, \dots), \tag{7}$$

or

$$P_1 P_3 - P_2^2 = \sum_{k=1}^{\infty} W_k(P_2 P_4 - P_3^2, P_3 P_5 - P_4^2, \dots). \tag{8}$$

This can be rewritten as

$$P_1 = P_2^2/P_3 + \sum_{k=1}^{\infty} W_k(P_2 P_4 - P_3^2, P_3 P_5 - P_4^2, \dots)/P_3. \tag{9}$$

Comparing this result with Eq. (5) we conclude that the expansion terms can be generated easily by means of the recursion

$$W_1 = P_2^2/P_3, \tag{10a}$$

$$\begin{aligned} W_{k+1}&(P_2, P_3, \dots) \\ &= P_3^{-1} W_k(P_2 P_4 - P_3^2, P_3 P_5 - P_4^2, \dots). \end{aligned} \tag{10b}$$

Pursuing this recursion, we obtain the following infinite expansion for E_0:

$$E_0 = I_1 - \frac{I_2^2}{I_3} - \left(\frac{1}{I_3}\right) \frac{(I_4 I_2 - I_3^2)^2}{I_5 I_3 - I_4^2} - \dots, \tag{11}$$

where the first five connected moments, Eq. (2), read

$$I_1 = \langle H \rangle, \tag{12}$$

$$I_2 = \langle H^2 \rangle - \langle H \rangle^2, \tag{13}$$

$$I_3 = \langle H^3 \rangle - 3\langle H^2 \rangle \langle H \rangle + 2\langle H \rangle^3, \tag{14}$$

$$I_4 = \langle H^4 \rangle - 4\langle H^3 \rangle \langle H \rangle - 3\langle H^2 \rangle^2 + 12\langle H^2 \rangle \langle H \rangle^2 - 6\langle H \rangle^4, \tag{15}$$

$$I_5 = \langle H^5 \rangle - 5\langle H^4 \rangle \langle H \rangle - 10\langle H^3 \rangle \langle H^2 \rangle + 20\langle H^3 \rangle \langle H \rangle^2 + 30\langle H^2 \rangle^2 \langle H \rangle - 60\langle H^2 \rangle \langle H \rangle^3 + 24\langle H \rangle^5. \tag{16}$$

Several properties of the connected-moments expansion (CMX), Eq. (11), have to be discussed. First, one should point out that the Kth order of CMX [CMX(K)], obtained by a truncation of the series (11) after the first K terms, requires the knowledge of $I_1, \dots, I_{2K+1}$. When these moments are available, construction of the CMX series up to any order is extremely easy because of the simplicity of the recursive algorithm (10). Another extremely important property, which can be easily proved by induction, is that the CMX series truncated at any order is always size extensive. This makes CMX particularly attractive for the many-body calculations. Also, the advantage of CMX over any perturbational technique is striking. There is no ambiguity in the partitioning of Hamiltonian and no problems with (quasi) degeneracy of the eigenfunctions of the unperturbed Hamiltonian. The CMX series, by virtue of the Horn-Weinstein theorem, is usually convergent, provided that the ket $|\phi\rangle$ has a nonzero overlap with the exact wave function. This makes it possible to utilize quite "crude" guesses for $|\phi\rangle$ that would probably ruin the convergence of perturbation theory.

The general character of CMX is confirmed by an independent derivation of similar series from the steepest-descent perturbation theory and from the Lanczos chain transformation.[3] In order to gain some insight into the applicability of the CMX approach, we carried out calculations for the hydrogen molecule within the 6-31G^{**} basis.[4] We tested the choices of both the relativistic Hartree-Fock (RHF) single determinant and the minimum 2×2 configuration-interaction (one RHF ground state + one doubly excited determinant) wave functions as the trial ket $|\phi\rangle$. For both choices of $|\phi\rangle$ we calculated the connected moments from the appropriate traces of matrices representing powers of the Hamiltonian and then invoked Eq. (11) to calculate the CMX terms. The basis-set correlation energy was calculated by a diagonalization of the single-double-excitation configuration-interaction matrix, which for the two-electron system is equivalent to a full configuration interaction. For the RHF zeroth-order function we performed additionally the calculations within the $MP3$ approach, which is one of the most popular techniques for estimation of the correlation energy of molecules.[2] The performance of all these methods was monitored for the H-H distances of R_e, $2R_e$, $5R_e$, and $10R_e$, where R_e is the equilibrium bond length of the singlet ground state of

TABLE I. Correlation energy (milihartrees) for the hydrogen molecule with various H-H distances ($R_e = 0.741$ Å). Values in parentheses refer to the fraction (%) of the basis-set correlation energy recovered.

H-H distance	R_e	$2R_e$	$5R_e$	$10R_e$
"Exact"	33.9	57.0	217.0	263.1
RHF wave function as $\lvert \phi \rangle$				
*MP*3	31.9(94)	45.1(79)	293.2(135)	861.9(328)
CMX(2)	25.6(76)	23.3(41)	46.7(22)	65.7(25)
CMX(3)	31.2(92)	45.3(79)	217.4(100)	344.6(131)
Two-determinant wave function as $\lvert \phi \rangle$				
Itself	5.1(15)	39.5(69)	203.6(94)	249.7(95)
CMX(2)	28.6(84)	51.6(91)	217.0(100)	263.2(100)
CMX(3)	32.7(97)	56.3(99)	217.0(100)	263.1(100)

H_2 (see Table I).

First we discuss results for the RHF trial function. From Table I we learn that for the bond lengths which do not differ significantly from R_e, both *MP*3 and CMX(2) perform quite well, recovering most of the basis-set correlation energy. The next rank of approximation, CMX(3), which is computationally as expensive as *MP*5, does not improve the CMX(2) results dramatically. However, for R values near the dissociation limit, the fraction of correlation energy calculated from CMX(2) is smaller and the use of CMX(3) does improve the results greatly, whereas *MP*3 overestimates the correlation energy to a great extent, because of quasidegeneracy of the eigenstates of the unperturbed Hamiltonian. From the above result it is clear that the CMX(2) approximation underestimates the correlation energy that comes from quasidegeneracy of states while *MP*3 tends to diverge in this case.

Next, we focus our attention on the results for the two-determinant function. This choice of $\lvert \phi \rangle$ resembles, in principle, the complete active space (CAS) self-consistent field (SCF) wave function.[5] For long H-H distances the trial function itself provides about 95% of the correlation energy and CMX(2) accounts accurately for the rest. For shorter distances CMX(2) improves greatly the calculated correlation energy, while the use of CMX(3) causes only minor changes.

From the above example we conclude that the CMX(2) approach can be of a real value when we deal with a multideterminant ground-state wave function such as CAS SCF[5] or the generalized valence-bond[6] one. For this kind of zeroth-order wave function, perturbational treatment has not been formulated yet and it seems that such a formulation could present some practical difficulties that would arise from the problem of partitioning of the Hamiltonian. The applicability of CMX(2) for calculation of the correlation energy for small molecules will be published elsewhere.[7]

Another test for the performance of CMX is the Maynau-Malrieu spin Hamiltonian This kind of Hamiltonian has been proposed recently as a convenient method for investigation of the electronic structure of π-conjugated systems.[8] Using the maximum-spin-alternation wave function as the trial ket we arrive at the average deviation (the sample of fifteen molecules) from the ground-state energy equal to 32.0%, 7.2%, and 4.2% for the CMX(1), CMX(2), and CMX(3) results, respectively.[9]

Although even at the present stage the new approach appears to be very promising, it is necessary to pursue further studies on the properties and applications of the CMX series. Two main routes seem to be especially interesting to explore: the formulation of CMX for multideterminant wave functions and study on the convergence rate of CMX. This work is in progress and results will be published in the near future.[10]

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