Cumulant-based calculations of the correlation energy in a molecule

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The problem of constructing a guaranteed convergent sequence of corrections to the Hartree–Fock ground state energy of a molecule without storing the many-electron wave function is considered. Several methods based on cumulants are considered and it is shown that such a sequence is obtained by Lanczos tridiagonalization, in which the elements of the tridiagonal matrix are calculated through cumulants.

The calculation of the correlation energy, defined as the difference between the exact energy of the electronic system and the approximate energy calculated by Hartree–Fock (HF) method, is a classic problem in quantum chemistry. The most straightforward way of the correlation energy calculation – full configuration interaction method (FCI) – leads to an exponential increase in the requirements for computer memory with an increase in the size of the molecule. The Møller–Plesset (MP) perturbation theory \[^{[1]}\] can do without such growth. To use this method, only Coulomb integrals and Hartree–Fock energy levels are needed \[^{[2]}\]. However, the resulting series may be divergent \[^{[3,4]}\].

Is it possible to build a guaranteed convergent method that requires comparable to MP? In the presented work, we will consider methods related to the calculation of cumulants, and give an affirmative answer to the question asked.

I. METHODS

A. Cumulant \(t\)-expansion

First, consider a method for finding the energy of the ground state, called the cumulant \(t\)-expansion \[^{[5]}\]. Given a Hamiltonian \(\hat{H}\) and an initial state \(|\phi_0\rangle\), let us define the moments

\[
\mu_m = \langle \phi_0 | \hat{H}^m | \phi_0 \rangle
\]

\(|\phi_0\rangle\) is normalized to unity) and introduce auxiliary function

\[
E(t) = \frac{\langle \phi_0 | \hat{H} e^{-\hat{H}t} | \phi_0 \rangle}{\langle \phi_0 | e^{-\hat{H}t} | \phi_0 \rangle}
\]

which can be written as a power series in the parameter \(t\):

\[
E(t) = \sum_{m=0}^{\infty} \frac{I_{m+1}}{m!} (-t)^m,
\]

where

\[
I_{m+1} = \mu_{m+1} - \sum_{p=0}^{m-1} \binom{m}{p} I_{p+1} \mu_{m-p}
\]

are the cumulants \[^{[6]}\] (note that in \[^{[7,8]}\] the values \(I_m\) were named “connected moments”). Then

\[
E_0 = \lim_{t \to \infty} E(t)
\]

is the minimal eigenvalue of the Schrödinger equation

\[
\hat{H} |\psi_0\rangle = E_0 |\psi_0\rangle
\]

provided that \(\langle \psi_0 | \phi_0 \rangle \neq 0\) (see \[^{[5]}\] for proof).

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Several ways have been proposed to calculate the limit using the first few known cumulants. In the papers, it was proposed to seek $E(t)$ as a sum of decaying exponentials, which leads to the following sequence of approximations for the ground state energy, called the connected moments expansion (CMX):

$$E_{0}^{\text{CMX}(n)} = I_1 - (I_2 \cdots I_n) \left( \begin{array}{cccc}
I_3 & \cdots & I_{n+1} \\
\vdots & \ddots & \vdots \\
I_{n+1} & \cdots & I_{2n-1} \\
\end{array} \right)^{-1} \begin{array}{c}
I_2 \\
\vdots \\
I_n
\end{array}. \tag{7}
$$

The CMX method was successfully tested on the problems of calculating the ground state energy of anharmonic oscillator and a hydrogen molecule. However, problems arose when trying to apply this method to many-electron lattice models: for some values of the model parameters, expression (7) became singular. In [5], the so-called $D$-Padé method was used, in which the Padé approximation is applied for the derivative of the $E$ function. In this case, the first two approximations to the sought ground state energy

$$E_{0}^{\text{DP}[0/M]} = I_1 - \int_0^{\infty} \frac{I_2}{Q_M(t)} dt,$$

where

$$Q_2(t) = 1 + \frac{I_3}{I_2} t + \frac{2I_4^2 - I_2 I_4}{2I_2^2} t^2,$$

$$Q_3(t) = 1 + \frac{I_3}{I_2} t + \frac{2I_4^2 - I_2 I_4}{2I_2^2} t^2 + \frac{6I_5^3 - 6I_2 I_3 I_4 + I_2^2 I_5}{6I_2^3} t^3$$

(for a more detailed description, see [14, 15]). However, it was shown in [15] that the $D$-Padé method is unsatisfactory in the whole range of parameters of the many-electron lattice Hubbard model.

Thus, the listed methods do not provide a guaranteed convergent sequence of approximations for the ground state energy.

B. Cumulant Lanczos tridiagonalization

Lanczos tridiagonalization (LT) is well known in computational many-electron physics. In this method the Hamiltonian is used to generate a sequence of orthonormal states $\{\phi_n\}_{n=1,2,\ldots}$ and Lanczos coefficients $\{\alpha_n\}_{n=0,1,\ldots,\beta_n\}_{n=1,2,\ldots}$ from a suitably chosen trial state $|\phi_0\rangle$ through the following recurrence

$$|\phi_{n+1}\rangle = \frac{1}{\beta_{n+1}} \left[ (\hat{H} - \alpha_n)|\phi_n\rangle - \beta_n|\phi_{n-1}\rangle \right], \tag{9}
$$

where $\alpha_n = \langle \phi_n | \hat{H} | \phi_n \rangle$, and $\beta_{n+1}$ — normalization factor ensuring the fulfillment of the condition $\langle \phi_{n+1} | \phi_{n+1}\rangle = 1$, so that the Hamiltonian in this new basis is tridiagonal [17]:

$$T_n = \begin{pmatrix}
\alpha_0 & \beta_1 \\
\beta_1 & \alpha_1 & \beta_2 \\
& \ddots & \ddots & \ddots \\
& & \beta_n & \alpha_n
\end{pmatrix}. \tag{10}
$$

The lowest eigenvalue $E_{0}^{LT(N)}$ of the matrix $T_{N-1}$ will be called the $N$th approximation ($N = 1, 2, \ldots$) to the ground state energy $E_0$. With increasing $N$, the expansion of the subspace spanned by the vectors $\{\phi_n\}_{n=0,\ldots,N-1}$ occurs, so $E_{0}^{LT(N)}$ can only decrease: $E_{0}^{LT(1)} \geq E_{0}^{LT(2)} \geq E_{0}^{LT(3)} \geq \cdots \geq E_0$. Thus, under the condition $\langle \psi_0 | \phi_0 \rangle \neq 0$ Lanczos tridiagonalization gives a monotonically decreasing, guaranteed convergent sequence of approximations to the true value of the ground state energy [15].

The main problem of traditional computational LT is the storage of states $\{\phi_n\}$ in the computer memory. And, typical for many-electron problems, the size of the memory required grows exponentially with the number of electrons. Instead, the first few elements of the matrix [10] can be expressed in terms of cumulants [18], which in many cases
can be calculated without storing many-electron states. First, we express $\alpha_n$ and $\beta_n$ in terms of moments $\mu_m$ [19]:

$$\alpha_n = \frac{\Delta'_n \Delta_n}{\Delta'_{n-1} \Delta_{n-1}} + \frac{\Delta'_n \Delta_{n-1}}{\Delta'_{n-1} \Delta_n},$$

$$\beta^2_n = \frac{\Delta_n \Delta_{n-2}}{\Delta'_{n-1}^2}$$

where

$$\Delta_n = \begin{vmatrix} \mu_0 & \mu_1 & \ldots & \mu_n \\ \mu_1 & \mu_2 & \ldots & \mu_{n+1} \\ \vdots & \vdots & \ddots & \vdots \\ \mu_n & \mu_{n+1} & \ldots & \mu_{2n} \end{vmatrix},$$

$$\Delta'_n = \begin{vmatrix} \mu_1 & \mu_2 & \ldots & \mu_{n+1} \\ \mu_2 & \mu_3 & \ldots & \mu_{n+2} \\ \vdots & \vdots & \ddots & \vdots \\ \mu_{n+1} & \mu_{n+2} & \ldots & \mu_{2n+1} \end{vmatrix}$$

and $\Delta_{-1} = 1, \Delta'_{-2} = 0, \Delta'_1 = 1$. Second, we write the moments in terms of cumulants according to [19]. And as a result

$$\alpha_0 = I_1,$$
$$\alpha_1 = I_1 + I_3/I_2,$$
$$\alpha_2 = I_1 + (I_3^2 - 2I_2I_3I_4 + I_2^2I_5 + 4I_2^3I_3)/( -I_2I_3^2 + I_2^2I_4 + 2I_2^4),$$
$$\beta^2_1 = I_2,$$
$$\beta^2_2 = 2I_2 + (-I_3^2 + I_2I_4)/I_2^2.$$

It remains to learn how to calculate cumulants without storing the many-electron state in the computer memory. This will be done below in relation to specific practical problems.

C. Convergence acceleration of a approximations sequence

It is advisable to accelerate the convergence of the obtained sequence $E_0^{LT(n)}$. Let’s apply the most popular $\varepsilon$-algorithm [20]. Let $S_n$ be some initial sequence ($n = 0, 1, \ldots$). For $k = 0, 1, \ldots$ we construct new sequences

$$\varepsilon^{(n)}_{k+1} = \varepsilon^{(n+1)}_{k+1} + \frac{1}{\varepsilon^{(n+1)}_k - \varepsilon^{(n)}_k},$$

where $\varepsilon^{(n)}_0 = S_n, \varepsilon^{(n)}_1 = 0$. Then, for a wide class of sequences $S_n$, it is true that the rate of convergence of sequences $\varepsilon^{(n)}_{2k}$ is the faster, the larger $k$.

Below, when applying this method, we will assume $S_n = E_0^{LT(n+1)}$.

II. APPLICATIONS

A. Anharmonic oscillator

Let us apply the described method to calculate the ground state energy of the anharmonic oscillator

$$\left( -\frac{1}{2} \frac{d^2}{dx^2} + \frac{x^2}{2} + gx^4 \right) |\psi_0\rangle = E_0 |\psi_0\rangle,$$

where, as is well known, the expansion in $g$ gives a diverging series [21].

In this case, the moments [11] can be calculated simply by the $n$-fold action of the Hamilton operator on the initial state $|\phi_0\rangle = e^{-x^2/2}$ followed by integration over $x$. Then $\alpha_n$ and $\beta_n$ are calculated using formulas [11], [12] and [13]. As expected, LT gives a monotonically converging sequence of approximations for all $g$. The convergence-accelerating $\varepsilon$-algorithm significantly improves the existing results.
TABLE I: The ground state energy $E_0$ of the anharmonic oscillator at different $g$

| $g$  | 0.1   | 0.3    | 0.5    | 1   | 2   |
|------|-------|--------|--------|-----|-----|
| $LT(1) = I_1$ | 0.575 | 0.725  | 0.875  | 1.25 | 2.875 |
| CMX(2) | 0.562940 | 0.670592 | 0.774160 | 1.029817 | 1.53846 |
| CMX(3) | 0.560608 | 0.655804 | 0.743471 | 0.955635 | 1.37375 |
| D-Pade[0/2] | 0.552529 | 0.603212 | 0.622528 | 0.601112 | 0.40048 |
| D-Pade[0/3] | 0.557691 | 0.640572 | 0.716298 | 1.031567 | 1.54249 |
| $LT(2)$ | 0.562969 | 0.670887 | 0.774834 | 1.031567 | 1.54249 |
| $LT(3)$ | 0.560621 | 0.656031 | 0.744094 | 0.957527 | 1.37849 |
| $LT(4)$ | 0.559802 | 0.649535 | 0.729617 | 0.920075 | 1.29192 |
| $LT(5)$ | 0.559459 | 0.646010 | 0.721307 | 0.897360 | 1.23757 |
| $LT(6)$ | 0.559304 | 0.643851 | 0.715955 | 0.882059 | 1.19991 |
| $LT(7)$ | 0.559230 | 0.642423 | 0.712242 | 0.871020 | 1.17206 |
| $\varepsilon(0)$ | 0.560051 | 0.650410 | 0.730482 | 0.919561 | 1.28687 |
| $\varepsilon(1)$ | 0.559364 | 0.644486 | 0.716732 | 0.881740 | 1.19509 |
| $\varepsilon(2)$ | 0.559212 | 0.641831 | 0.701054 | 0.862348 | 1.14596 |
| $\varepsilon(3)$ | 0.559176 | 0.640434 | 0.702826 | 0.850479 | 1.11484 |
| $\varepsilon(4)$ | 0.559162 | 0.639632 | 0.703826 | 0.842436 | 1.09313 |
| $\varepsilon(5)$ | 0.559195 | 0.641091 | 0.708015 | 0.855645 | 1.12802 |
| $\varepsilon(6)$ | 0.559168 | 0.639698 | 0.703911 | 0.842350 | 1.09229 |
| $\varepsilon(7)$ | 0.559156 | 0.639027 | 0.701596 | 0.834198 | 1.06954 |
| exact(22) | 0.559146 | 0.637992 | 0.696176 | 0.803771 | 0.95157 |

B. Correlation energy in a molecule

One of the first attempts to use cumulant expansions in quantum chemistry has been made in \cite{7}. In this work, the cumulants were calculated from the appropriated traces of matrices representing powers of Hamiltonian. This method requires the use of all many-electron configurations, so as expensive as the FCI. But for practical purposes, the cumulants need to be calculated in more economical way. Such a calculation (by pairing technique) of cumulants up to third order was carried out in \cite{23}, but using CMX(2) only about half of the correlation energy was captured.

In this work, we have derived formulas for cumulants up to the fifth order using the technique described below. Suppose that the Hartree–Fock equations for a molecule are written and solved by standard methods. Let us write the Hamiltonian of the problem in the second quantization representation \cite{24} using solutions of the restricted Hartree–Fock (RHF) equations $\chi_i(r)$ as single-electron states:

$$
\hat{H} = \sum_{i\sigma} \varepsilon_i c_{i\sigma}^\dagger c_{i\sigma} - \sum_{ij\sigma\sigma'} (2[ij|\gamma\gamma] - [i\gamma|\gamma j]) c_{i\sigma}^\dagger c_{j\sigma'} + \frac{1}{2} \sum_{ijkl\sigma\sigma'} [ij|kl] c_{i\sigma}^\dagger c_{k\sigma'} c_{l\sigma'} c_{j\sigma} ,
$$

(17)

where summation over $\gamma$ is carried out over occupied orbitals, $\varepsilon_i$ – the energy of the $i$th orbital and Coulomb integrals

$$
[ij|kl] = \int \chi_i^*(r_1) \chi_j(r_1) \frac{1}{r_{12}} \chi_k^*(r_2) \chi_l(r_2) dr_1 dr_2 .
$$

(18)

For the initial ket $|\phi_0\rangle$ being the RHF wavefunction, $I_1$ is the Hartree–Fock energy, and other cumulants can be calculated using Wick’s pairing technique (for more details see \cite{14, 15}). Performing necessary analytical calculations,
we have obtained the final expressions for cumulants:

\[ I_2 = \sum_{abr^*s^*} [ar|bs] \cdot (2[ar|bs] - [as|br]) \]
\[ I_3 = \sum_{abr^*s^*} 2[ar|bs] \cdot (2[ar|bs] - [as|br]) \cdot (\varepsilon_r - \varepsilon_a) \]
\[ + \sum_{abcr^*s^*t^*} 2[ar|bs] \cdot [2[ar|ct](2[bs|ct] - [bt|cs]) - [br|ct](2[as|ct]) - [at|cs] - [rt|ca](2[at|bu] - [au|bt]) \]
\[ + \sum_{abcr^*s^*t^*} [ar|bs][ac|bd](2[cr|ds] - [dr|cs]) \]

where the starred (unstarred) indices refer to virtual (occupied) orbitals. It should be noted that the derived formulas differ from those given in [23]: the term with the sum over \(abcr^*s^*t^*\) is different, while the rest terms coincide with those calculated in the indicated work. Apparently, an error was made in this article when deriving the formula for \(I_3\). At the same time, the results of calculations using our formulas [19] completely coincide with the results obtained by direct computation of the traces of the Hamiltonian power matrices.

The explicit formulas for cumulants \(I_4\) and \(I_5\) were obtained using a program for analytical calculations, but are not given here because of their large size (in particular, the expression for \(I_4\) contains more than two hundred lines).

As an illustration, the correlation energy of a hydrogen molecule was calculated within the 6-31** basis. The results of ground state energy calculations using the described technique are presented in Table II.

**TABLE II:** Ground state energy (hartrees) for the hydrogen molecule with 1.4 a.u. H–H distance; third column: captured part of the correlation energy

| Method     | Energy     | Captured Part (%) |
|------------|------------|-------------------|
| HF         | -1.131287  |                   |
| MP2        | -1.157629  | 77.8%             |
| MP3        | -1.162488  | 92.1%             |
| CMX(2)     | -1.156932  | 75.7%             |
| CMX(3)     | -1.162512  | 92.2%             |
| D-Pade[0/2]| -1.175371  | 130.1%            |
| D-Pade[0/3]| -1.166466  | 103.9%            |
| LT(2)      | -1.156769  | 75.2%             |
| LT(3)      | -1.162338  | 91.7%             |
| \(\varepsilon_0\) | -1.163895 | 96.3%             |
| FCI        | -1.165159  |                   |

Thus, cumulant Lanczos tridiagonalization, being comparable in terms of resource requirements with the Møller–Plesset perturbation theory, yield a guaranteed convergent, monotonic sequence of approximations to the correlation energy. I would like to draw the attention of researchers to this method.

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