Brief Reports

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Connected moments expansion for the ground-state energy of systems described by nonlinear Hamiltonians

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An extension of the connected moments expansion to nonlinear Hamiltonians is presented. The new method enables construction of rapidly convergent series for the ground-state energy which requires a relatively small amount of numerical effort.

Nonlinear effective Hamiltonians are useful in several branches of quantum physics and chemistry. In particular, the nonlinear Schrödinger equation

$$\hat{H}\,|\,\phi\rangle = E\,|\,\phi\rangle \tag{1}$$

with the Hamiltonian of the form

$$\hat{H} = \hat{H}_0 + \sum_{i=1}^{N} \alpha_i \langle A_i \rangle \hat{B}_i \ , \tag{2}$$

where

$$\langle A \rangle = \langle \phi \,|\, \hat{A} \,|\, \phi \rangle \tag{3}$$

and α_i are the respective coupling constants, describes the molecule-solvent interactions[1-3] and therefore is of great interest for physical chemistry.

Solution of the nonlinear problem (1) is usually accomplished by iteration of a linearized Hamiltonian eigenproblem or by application of the perturbation theory.[4] The first approach suffers from its numerical rather than algebraic character, whereas the second one is plagued by the usual shortcomings of the perturbation theory, namely, complicated formulas and problems with convergence for large perturbations. Size extensivity of the calculated energy is not guaranteed, as no analog of the linked-clusters theorem[5] is known for the nonlinear perturbation theory.

Very recently a new method for the solution of many-body problems has been developed. The connected moments expansion (CMX) provides a rapidly convergent series for the ground[6-8] as well as the excitation energies.[7] Within the CMX approach, a proper handling of the size extensivity is extremely easy to achieve and the calculation of the energy requires a rather modest amount of numerical effort. Having all those advantages in mind, we present here an extension of the CMX approach to the systems described by the nonlinear Hamiltonians of the form given by Eq. (2). Generalization to other forms is straightforward and therefore will not be given here.

Let $|\,Q\rangle$ be a trial ket having a nonzero overlap with the exact wave function of the ground state. The wavefunction

$$|\,Q_t\rangle = \langle Q \,|\, \exp(-t\hat{H}) \,|\, Q\rangle^{-1/2} \exp(-t\hat{H}/2) \,|\, Q\rangle \tag{4}$$

converges to the ground-state eigenfunction as t approaches infinity.[9] Similarly, the function

$$F(\hat{A},t) = \langle Q_t \,|\, \hat{A} \,|\, Q_t \rangle \tag{5}$$

conforms to the limit

$$\lim_{t\to\infty} F(\hat{A},t) = \langle A \rangle \tag{6}$$

for any operator $\hat{A}$ having a finite expectation value $\langle A \rangle$.

Taking into account the Taylor expansion of the exponential operator in Eq. (4), we arrive at the series representation for the function $F(\hat{A},t)$:

$$F(\hat{A},t) = \sum_{j=0}^{\infty} (-t)^j I_{j+1}(\hat{A})/j! \ , \tag{7}$$

where the generalized connected moments $I_k(\hat{A})$ are defined recursively as

$$I_1(\hat{A}) = b_1(\hat{A}) \ , \tag{8a}$$

$$I_j(\hat{A}) = b_j(\hat{A}) - \sum_{k=1}^{j-1} \begin{bmatrix} j-1 \\ k-1 \end{bmatrix} I_k(\hat{A}) \langle Q \,|\, \hat{H}^{j-k} \,|\, Q \rangle \ , \tag{8b}$$

TABLE I. Exact [Eq. (15)] and approximate [Eqs. (19)–(22)] energies of the ground state of the nonlinear harmonic oscillator [Eq. (14)].

α	E_{ex}	$E_{(1,1)}$	$E_{(1,2)}$	$E_{(2,1)}$	$E_{(2,2)}$
0.01	0.502 482	0.502 500	0.502 488	0.502 493	0.502 485
0.02	0.504 927	0.505 000	0.504 951	0.504 975	0.504 939
0.05	0.512 060	0.512 500	0.512 199	0.512 348	0.512 126
0.10	0.523 340	0.525 000	0.523 836	0.524 405	0.523 565
0.20	0.544 017	0.550 000	0.545 636	0.547 727	0.544 681
0.50	0.595 744	0.625 000	0.601 884	0.612 500	0.597 573
1.00	0.662 359	0.750 000	0.675 391	0.708 333	0.664 004

and the generalized moments b_j read

$$b_j(\hat{A})=2^{-(j-1)}\sum_{k=0}^{j-1}\binom{j-1}{k}\langle Q\mid \hat{H}^k\hat{A}\hat{H}^{j-k-1}\mid Q\rangle \ . \quad (9)$$

For the operator $\hat{A}$ being the Hamiltonian, the above formulas reduce to those for connected moments of the Hamiltonian.[6,7,9]

With the knowledge of a limited number of connected moments it is possible to obtain approximations to the limits (6).[6–8] The nth order approximation to the observables associated with the Hamiltonian (2) reads

$$\langle A_i\rangle_n=I_1(\hat{A}_i)-[I_2(\hat{A}_i),\ldots,I_n(\hat{A}_i)]\begin{bmatrix} I_3(\hat{A}_i) & \cdots & I_{n+1}(\hat{A}_i)\\ \cdots & \cdots & \cdots\\ I_{n+1}(\hat{A}_i) & \cdots & I_{2n-1}(\hat{A}_i)\end{bmatrix}^{-1}\begin{bmatrix} I_2(\hat{A}_i)\\ \cdots\\ I_n(\hat{A}_i)\end{bmatrix} \ . \quad (10)$$

By analogy, the ground-state energy is approximated to nth order by

$$E_n=I_1(\hat{H})-[I_2(\hat{H}),\ldots,I_n(\hat{H})]\begin{bmatrix} I_3(\hat{H}) & \cdots & I_{n+1}(\hat{H})\\ \cdots & \cdots & \cdots\\ I_{n+1}(\hat{H}) & \cdots & I_{2n-1}(\hat{H})\end{bmatrix}^{-1}\begin{bmatrix} I_2(\hat{H})\\ \cdots\\ I_n(\hat{H})\end{bmatrix} \ . \quad (11)$$

If all the (modified) connected moments are finite, then[6–8]

$$\lim_{n\to\infty}\langle A_i\rangle_n=\langle A_i\rangle \ , \quad i=1,\ldots,N \quad (12)$$

and

$$\lim_{n\to\infty}E_n=E \ . \quad (13)$$

Equations (8)–(11) form a conceptual basis for the CMX approach to the solution of nonlinear problem (1). To calculate an approximate ground-state energy, one has to compute a set of modified connected moments, Eqs. (8) and (9), for the Hamiltonian and all the operators $\hat{A}_i, i=1,\ldots,N$. The next step is to approximate the values of associated observables, $\langle A_i\rangle$, Eq. (10). Because the modified connected moments themselves depend on $\langle A_i\rangle$, one has to solve a system of nonlinear equations to calculate the observables. This can be done easily using algebraic methods (for lower orders of CMX) or the Newton algorithm. Finally, having computed $\langle A_i\rangle$, we calculate an approximate ground-state energy from Eq. (11). We denote the rank of approximation by CMX $(m,n_1,n_2,\ldots)$ where the energy was calculated up to mth order, and $\langle A_1\rangle,\langle A_2\rangle,\ldots$ were calculated up to their n_1th, n_2th, ... orders.

To illustrate the above considerations we present calculations for the Hamiltonian describing a harmonic oscillator with the force constant depending on the mean square of the amplitude of vibration:

$$\hat{H}=(-\tfrac{1}{2})d^2/dx^2+(x^2/2)+\alpha\langle x^2\rangle x^2 \ . \quad (14)$$

The exact values of E and the associated observable $\langle x^2\rangle$ can be easily calculated from the relations

$$8E^3-2E-\alpha=0 \quad (15)$$

and

$$\langle x^2\rangle=(4E)^{-1} \ , \quad (16)$$

whereas the approximate values are given by

$$\langle x^2\rangle_{(1)}=\tfrac{1}{2} \ , \quad (17)$$

$$\langle x^2\rangle_{(2)}=\{[(4+\alpha)^2+16\alpha]^{1/2}-(4+\alpha)\}/(4\alpha) \ , \quad (18)$$

$$E_{(1,1)}=(2+\alpha)/4 \ , \quad (19)$$

$$E_{(2,1)}=(2+\alpha)/4-(\tfrac{1}{8})\alpha^2/(2+\alpha) \ , \quad (20)$$

$$E_{(1,2)}=\tfrac{1}{2}+(\tfrac{1}{8})\{[(4+\alpha)^2+16\alpha]^{1/2}-(4+\alpha)\} \ , \quad (21)$$

$$E_{(2,2)}=\tfrac{1}{2}+(\tfrac{1}{8})\{[(4+\alpha)^2+16\alpha]^{1/2}-(4+\alpha)\}$$
$$-(\tfrac{1}{32})\{[(4+\alpha)^2+16\alpha]^{1/2}$$
$$-(4+\alpha)\}^2/\{[(4+\alpha)^2+16\alpha]^{1/2}-\alpha\}\ , \quad (22)$$

for the wave function describing the ground state of an unperturbed ($\alpha=0$) oscillator chosen as the trial ket $|Q\rangle$. In Tables I and II we compare all those numbers with the exact ones.

The example, although slightly artificial, illustrates conveniently the major features of the CMX approximation. The CMX(1,1) energy, equivalent to the one calculated within first-order perturbation theory, diverges from the exact energy even for small α. The CMX(1,2) result accounts for the second order $\langle x^2\rangle$, but the energy itself is calculated only up to first order. On the other hand, the CMX(2,1) result includes second-order effects on the energy, calculated with an unperturbed value of $\langle x^2\rangle$. Both CMX(1,2) and CMX(2,1) energies are superior to the CMX(1,1) result; however, the CMX(2,2) energy compares the most favorably with the exact one, since it incorporates the second-order effect on the energy and the value of $\langle x^2\rangle$.

TABLE II. Exact [Eq. (16)] and second order [Eq. (18)] values of $\langle x^2\rangle$.

α	$\langle x^2\rangle_{ex}$	$\langle x^2\rangle_{(2)}$
0.01	0.497 531	0.497 518
0.02	0.495 121	0.495 074
0.05	0.488 224	0.487 948
0.10	0.477 701	0.476 719
0.20	0.459 545	0.456 356
0.50	0.419 643	0.407 537
1.00	0.377 439	0.350 781

It is possible to expand the exact energy, Eq. (15), as a Taylor series around the point $\alpha=0$ which yields the coefficients of the perturbation series. Inspection of those results reveals that the perturbation theory gives in this case very unsatisfactory results and probably diverges in higher orders. Having in mind the above example as well as all the advantages of the CMX approach, we hope that the new method will find widespread applications in nonlinear problems of quantum theory.

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