Linear Jahn-Teller effect: A connected-moments approach

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(Received 18 November 1996)

The ground-state energy of the linear $E\otimes\epsilon$ Jahn-Teller effect is obtained using a connected-moments expansion. The calculation is straightforward and leads to a set of simple algebraic expressions for the connected moments of the Hamiltonian. This is then compared to a recent calculation wherein a coupled-cluster scheme has been applied resulting in a set of thirteen nonlinear coupled algebraic equations. [S0163-1829(97)06230-9]

Interest in the dynamical Jahn-Teller effect by both chemists and physicists has remained consistent for the past few decades.[1,2] Systems which exhibit such behavior present not only a number of theoretical complexities, but also are of thermodynamic interest as they display nonadiabatic behavior.[3] The simplest nontrivial example of such a system is the linear $E\otimes\epsilon$ Jahn-Teller effect wherein a double-degenerate electronic level is coupled to two degenerate oscillators.[4–11] One such environment in which this system may be found is if there exists a foreign ion embedded in a trigonal or hexagonal host crystal or molecule as in the complex AgCl:Fe^{2+}. Further interest in certain aspects of the Jahn-Teller effect has come to the fore as a possible physical mechanism for high-temperature superconductors.[12–15]

A complete numerical solution of the linear $E\otimes\epsilon$ system has been known for a number of years.[5] However, interest in analytic methods applied to this system has not waned. In fact, this has provided fertile testing grounds for a number of analytic methods, among which are canonical transformations and variational calculations.[7–10,16–18] Most recently, Wong and Lo[19] have applied the successive coupled-cluster method (CCM) up to the third level in order to study the ground state of the linear $E\otimes\epsilon$ effect. Their results are valid throughout parameter space and give excellent agreement with both exact numerical diagonalization results and also other analytic studies. The CCM represents a readily understandable and systematic approximation scheme[20] and has recently been applied to Heisenberg-type spin systems[21] as well as the two-level periodic Anderson lattice.[22]

Although mathematically straightforward, the set of equations generalized by the CCM can in fact become quite tedious and involved. In their work, in which they claim that the mathematical treatment is ''quite simple,'' Wong and Lo[19] need to solve 13 nonlinear coupled algebraic equations. In general, these equations have no closed-form solutions and must be solved using numerical methods.

In this paper, we wish to study the ground state of the linear $E\otimes\epsilon$ Jahn-Teller effect using the connected-moments expansion (CMX) as developed by Cioslowski.[23] This scheme has been applied to a number of many-body Hamiltonian systems with varying degrees of success.[24–27] There are a number of motivating factors for using the CMX, among which is the fact that it is size extensive, usually convergent, and trivial to program. Furthermore, the necessary algebra for the linear $E\otimes\epsilon$ system may be generated manually in a few hours. This is in stark contrast to the myriad to equations generated by the CCM.

The third-order CMX expression for the ground-state energy is given by[23]

$$E_0^{\mathrm{CMX}(3)}=I_1-\frac{I_2^2}{I_3}-\frac{1}{I_3}\frac{(I_2I_4-I_3^2)^2}{I_3I_5-I_4^2}\cdots . \tag{1}$$

Here the connected moments I_k of the Hamiltonian are given by

$$I_k=\langle H^k\rangle-\sum_{i=0}^{k-2}\begin{bmatrix}k-1\\ i\end{bmatrix}I_{i+1}\langle H^{j-i-1}\rangle, \tag{2}$$

with $\langle H^k\rangle\equiv\langle\Psi_0|H^k|\Psi_0\rangle$.

We shall also calculate the ground-state energy as given by the recently developed alternate-moments expansion (AMX).[28] To second-order we have

$$E_0^{\mathrm{AMX}(2)}=I_1-\frac{I_2I_3}{I_4}, \tag{3}$$

with the I_k defined above.

Explicitly, the Hamiltonian for the linear $E\otimes\epsilon$ Jahn-Teller system is given in second-quantized notation by

$$H=a_1^\dagger a_1+a_2^\dagger a_2+1-\frac{k}{\sqrt{2}}(a_1^\dagger+a_1)\sigma_z+\frac{k}{\sqrt{2}}(a_2^\dagger+a_2)\sigma_x, \tag{4}$$

where $a_1^\dagger(a_1)$ and $a_2^\dagger(a_2)$ are boson creation (annhilation) operators and the σ_x and the σ_z are Pauli spin matrices.

Following Ref. 19, we shall transform the Hamiltonian given by Eq. (4) according to the prescription

$$\hat{H}=\exp(T^{\dagger})H\ \exp(T), \tag{5}$$

with

$$T=\frac{k}{\sqrt{2}}\,(a_1^{\dagger}-a_1). \tag{6}$$

The result is

$$\hat{H}=a_1^{\dagger}a_1+a_2^{\dagger}a_2+1+\eta(a_1^{\dagger}+a_1)(1-2S_z)+\eta(a_2^{\dagger}+a_2)(S_{+}+S_{-}), \tag{7}$$

where $\eta=k/\sqrt{2}$ and S_Z and $S_{\pm}$ are the usual spin opertors. In order to explicitly evaluate the connected moments and hence obtain the ground-state energy, we shall need to choose an initial trial vector. In order to make direct comparison, we again follow Wong and Lo[19] and choose

$$|\Psi_0\rangle=|\mathrm{vac}\rangle|\uparrow\rangle. \tag{8}$$

As was mentioned above, the algebra within this scheme is trivial and may be done manually in a few hours. We summarize our results below. Powers of the Hamiltonian matrix are expressed as function of the parameter η as

$$\begin{aligned}\langle H\rangle&=1-\eta^2,\\ \langle H^2\rangle&=1-\eta^2+\eta^4,\\ \langle H^3\rangle&=1+\eta^2+4\eta^4-\eta^6,\\ \langle H^4\rangle&=1+7\eta^2+20\eta^4+2\eta^6+\eta^8,\\ \langle H^5\rangle&=1+2l\eta^2+98\eta^4+72\eta^6+19\eta^8-\eta^{10}.\end{aligned} \tag{9}$$

The first five connected moments may be written explicitly using Eq. (2):

$$\begin{aligned}I_1&=\langle H\rangle,\\ I_2&=\langle H^2\rangle-\langle H\rangle^2,\\ I_3&=\langle H^3\rangle-3\langle H^2\rangle\langle H\rangle+2\langle H\rangle^3,\\ I_4&=\langle H^4\rangle-4\langle H^3\rangle\langle H\rangle-3\langle H^2\rangle^2+12\langle H^2\rangle\langle H\rangle^2-6\langle H\rangle^4,\\ I_5&=\langle H^5\rangle-5\langle H^4\rangle\langle H\rangle-10\langle H^3\rangle\langle H^2\rangle+20\langle H^3\rangle\langle H\rangle^2\\ &\quad+30\langle H^2\rangle^2\langle H\rangle-60\langle H^2\rangle\langle H\rangle^3+24\langle H\rangle^5.\end{aligned} \tag{10}$$

In Fig. 1 we have plotted the connected moments I_k. This is of interest so that the nature of the singularities which appear in Eqs. (1) and (3) might be investigated. Such singularities are well known to plague moments schemes[29] and indeed for certain many-body Hamiltonian systems yield results for the ground-state energy which are intractable.[11,24,26] For the linear $E\otimes e$ system, our results for the ground-state energy are void of such troubling points. This demonstrates once again that the schemes derived from Cioslowski work best for atomic and molecular Hamiltonian systems rather than true many-body ones. This is evident in Fig. 2 which

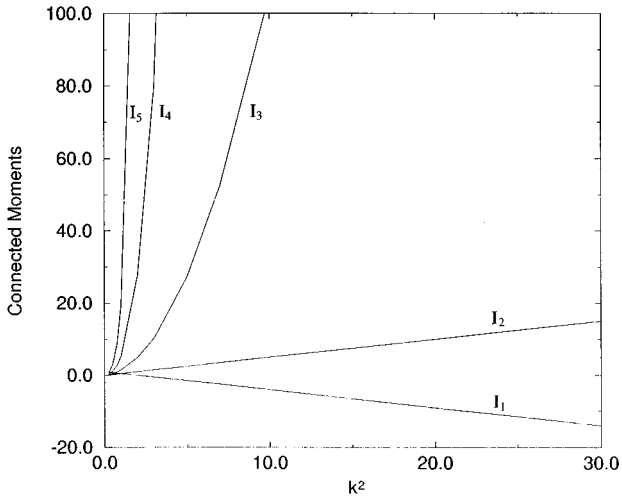

FIG. 1. First five connected moments are plotted as a function of the parameter k^2. We note the absence of singularities which is well known to plague moments.

represents our main results. Here we have plotted the percent error in ground-state energy values obtained using CMX(2), CMX(3), and AMX(2) expressions and compared them to the results in Ref. 19. We find that estimations using moments expansion schemes up to the second order [CMX(2) and AMX(2)] are similar to the first-order coupled-cluster approach. The CMX(3) result lies in between CCM(2) and CCM(3), all in reasonable agreement with the exact result throughout parameter space. Further calculational effort to investigate CMX(4) and AMX(3) would require the evaluation of matrix elements of the Hamiltonian to order $\langle H^6\rangle$ and $\langle H^7\rangle$ and would necessarily improve the agreement with Ref. 19. This is a straightforward matter and requires the evaluation of long strings of second-quantized operators. Improved agreement with exact results may also be achieved by choosing an initial trial vector which has maximal overlap with the true ground-state wave function in Hilbert space.

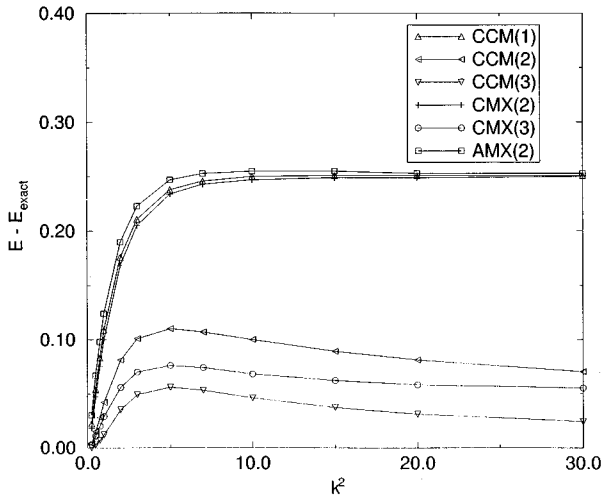

FIG. 2. Error in the ground-state energy is plotted using CMX(2), CMX(3), and AMX(2) expressions and comparing them to the results of Ref. 19.

To conclude, it was found that using a moments expansion with a minimum calculational effort, excellent agreement with the more tedious coupled-cluster scheme may be achieved for the linear $E \otimes \epsilon$ Jahn-Teller effect. Our finding that such schemes work well for atomic and molecular systems is consistent with earlier work. The simplicity of the method should serve as a model for future calculations in this area.

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