Coupled-cluster approximation for the linear E-e Jahn-Teller effect

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The successive coupled-cluster approximation up to the third level is applied to study the ground state of the linear E-e Jahn-Teller effect. Over the whole range of the coupling parameter, our results for the ground-state energy are not only in good agreement with the exact numerical diagonalization results, but they are also better than those from earlier analytical studies. The mathematical treatment in this work is quite simple and could be easily extended to the studies of the more complicated Jahn-Teller systems.

In recent years, a lot of attention has been paid to the studies of the dynamical Jahn-Teller effect in localized systems because of the growing number of experimental manifestations of the Jahn-Teller effect in molecules and solids.[1,2] Among the various Jahn-Teller systems, the linear E-e system, i.e., an electronic doublet interacting with a doubly degenerate vibration, is the simplest but nontrivial one, and has been completely solved by numerical methods many years ago.[3,4] However, there has been continued interest in approximate analytical solutions, because analytical methods are usually able to provide more physical insight than numerical methods and can be extended to more complicated cases, e.g., the multimode case, the nonlinear effects, and the cooperative systems, where numerical methods are very difficult to apply. Previous analytical treatments of the linear E-e Jahn-Teller system are either based on canonical transformations or on the variational principle.[5–12] In this communication, we explore the applicability of the coupled-cluster method to the ground state of the linear E-e Jahn-Teller system. The coupled-cluster method has proved to be a very useful technique, and has been applied to a wide range of physical systems in nuclear physics, quantum chemistry, relativistic quantum field theory, etc.[13] One of its main advantages is its systematic ability to be taken to arbitrary accuracy. The coupled-cluster method can be used to calculate ground-state and excited-state energies, and also such other physical quantities as correlation functions and density matrices.

The basic ideas of the coupled-cluster method rely on the fact that the exact ground state of a system described by the Hamiltonian H can always be expressed as

$$|\Psi\rangle = \exp(S)|\Phi_0\rangle , \qquad (1)$$

with $|\Phi_0\rangle$ being an appropriate "starting wave function" which is not orthogonal to the exact ground state. The corresponding Schrödinger equation

$$H|\Psi\rangle = E_0|\Psi\rangle , \qquad (2)$$

can then be written as

$$\mathcal{H}|\Phi_0\rangle \equiv \exp(-S)H \exp(S)|\Phi_0\rangle = E_0|\Phi_0\rangle , \qquad (3)$$

where

$$\exp(-S)H \exp(S) = H + [H,S] + \frac{1}{2}[[H,S],S] + \cdots . \qquad (4)$$

Since $|\Phi_0\rangle$ is normalized, we may write

$$E_0 = \langle\Phi_0|\mathcal{H}|\Phi_0\rangle = \langle\Phi_0|\exp(-S)H \exp(S)|\Phi_0\rangle , \qquad (5)$$

and by projecting Eq. (3) onto the states $|\Phi_n\rangle$ which are orthogonal to $|\Phi_0\rangle$, we obtain

$$\langle\Phi_n|\mathcal{H}|\Phi_0\rangle = \langle\Phi_n|\exp(-S)H \exp(S)|\Phi_0\rangle = 0 . \qquad (6)$$

This orthogonality condition yields a series of nonlinear coupled equations, each of which contains a finite number of terms. The correlation operator S is determined by solving these equations. Once S is known, the ground-state energy and wave function can be obtained readily. Hence, the problem of finding the ground-state energy and wave function of the system is reduced to computing the operator S. Nevertheless, this is a very formidable task, and some approximation scheme has to be used to solve the coupled equations. In the following, we shall apply a successive coupled-cluster approximation scheme to investigate the ground state of the linear E-e Jahn-Teller system. This approximation scheme has been successfully applied to the quantum spin systems and Hubbard model on a square lattice.[14–17]

The linear E-e Jahn-Teller system is described by the Hamiltonian,

$$H = a_1^\dagger a_1 + a_2^\dagger a_2 + 1 - \frac{k}{\sqrt{2}}(a_1^\dagger + a_1)\sigma_z + \frac{k}{\sqrt{2}}(a_2^\dagger + a_2)\sigma_x , \qquad (7)$$

where $a_1^\dagger(a_1)$ and $a_2^\dagger(a_2)$ are boson creation (annihilation) operators, and σ_x and σ_z are the usual Pauli matrices. We begin our treatment by first applying a unitary displacement transformation to H: $\tilde{H} = \exp(T^\dagger)H\exp(T)$, where $T = (k/\sqrt{2})(a_1^\dagger - a_1)$. After the transformation, we obtain

$$\tilde{H} = a_1^\dagger a_1 + a_2^\dagger a_2 + 1 + \eta^2(1 - 4S_z)$$
$$+ \eta(a_1^\dagger + a_1)(1 - 2S_z) + \eta(a_2^\dagger + a_2)(S_+ + S_-) ,$$
$$(8)$$

where $\eta = k/\sqrt{2}$. The operators S_z and $S_\pm$ are the spin operators corresponding to the Pauli matrices. To initiate our coupled-cluster approximation, we choose our "starting state" $|\Phi_0\rangle$ to be the state $|\mathrm{vac}\rangle| \uparrow\rangle$. This "starting state" has the advantage that if we apply the $\tilde{H}$ to this state, the off-diagonal term $\eta(a_1^\dagger + a_1)(1 - 2S_z)$ will vanish automatically. With this $|\Phi_0\rangle$, we simply choose the correlation factor S in Eq. (1) to be $\alpha a_2^\dagger S_-$ for the first level of the successive coupled-cluster approximation. This operator simply represents the simultaneous excitation of the spin and the vibrational mode 2. Using this correlation operator S, it can be found that

$$\mathcal{H}|\Phi_0\rangle = \{ E_0 + FS + \eta\alpha a_2^{\dagger 2}$$
$$+ 2\eta\alpha a_1^\dagger a_2^\dagger S_- - \eta\alpha^2 a_2^{\dagger 3} S_- \}|\Phi_0\rangle , \quad (9)$$

where $\mathcal{H} = \exp(-S)\tilde{H}\exp(S)$, $E_0 = 1 - \eta^2 + \eta\alpha$, and $\alpha F = \eta + (1 + 4\eta^2)\alpha - \eta\alpha^2$. By setting F to be zero, a quadratic equation of the parameter α is obtained, which can be easily solved to give two roots. The admissible solution is given by $\alpha = (1 + 4\eta^2 - \sqrt{1 + 12\eta^2 + 16\eta^4})/(2\eta)$. With the remaining terms of Eq. (9) being neglected, an estimate of the ground-state energy is found to be $E_0 = 1 - \eta^2 + (1 + 4\eta^2 - \sqrt{1 + 12\eta^2 + 16\eta^4})/2$.

Next, in order to improve the approximation, we shall include in S all the terms necessary to cancel the remaining terms of Eq. (9): $S = \sum_{n=1}^4 S_n$ with $S_1 = \alpha_1 a_2^\dagger S_-$, $S_2 = \alpha_2 a_1^\dagger a_2^\dagger S_-$, $S_3 = \alpha_3 a_2^{\dagger 2}$, and $S_4 = \alpha_4 a_2^{\dagger 3} S_-$. The terms S_1 and S_4 denote simultaneous excitations of the spin and the vibrational mode 2, S_2 the simultaneous excitation of the spin and both of the vibrational modes, and S_3 the excitation of the mode 2 only. With this correlation operator S, we obtain a set of four nonlinear coupled algebraic equations of the parameters α_i's:

$$\eta\alpha_1^2 - (1 + 4\eta^2)\alpha_1 - 2\eta(\alpha_2 + \alpha_3) - \eta = 0 ,$$
$$\eta\alpha_1 + 3\eta\alpha_4 + (1 + 2\eta\alpha_1)\alpha_3 = 0 ,$$
$$\eta\alpha_1 + (1 - \eta\alpha_1 + 2\eta^2)\alpha_2 = 0 ,$$
$$\eta(1 + 2\alpha_3)\alpha_1^2 - (3 - 4\eta\alpha_1 + 4\eta^2)\alpha_4 = 0 . \quad (10)$$

These nonlinear coupled equations have no closed-form solutions, in general, and need to be solved numerically. At this second level of approximation the ground-state energy is given by $E_0 = 1 - \eta^2 + \eta\alpha_1$. It is obvious that provided the parameters α_2, α_3, and α_4 are not zero, there is considerable improvement beyond the first-level results (see Table I). Finally, to go to the third-level approximation, we shall repeat the previous procedure and choose the correlation operator S as follows:

$$S = \sum_{n=1}^{13} S_n , \quad (11)$$

where

$$S_1 = \alpha_1 a_2^\dagger S_- , \quad S_2 = \alpha_2 a_1^\dagger a_2^\dagger S_- , \quad S_3 = \alpha_3 a_2^{\dagger 2} ,$$
$$S_4 = \alpha_4 a_2^{\dagger 3} S_- , \quad S_5 = \alpha_5 a_1^{\dagger 2} a_2^\dagger S_- ,$$
$$S_6 = \alpha_6 a_1^\dagger a_2^{\dagger 3} S_- , S_7 = \alpha_7 a_1^\dagger , \quad S_8 = \alpha_8 a_1^\dagger a_2^{\dagger 2} ,$$
$$S_9 = \alpha_9 a_2^{\dagger 4} , S_{10} = \alpha_{10} a_2^{\dagger 5} S_- , \quad S_{11} = \alpha_{11} a_1^\dagger a_2^{\dagger 5} S_- ,$$
$$S_{12} = \alpha_{12} a_1^{\dagger 2} a_2^{\dagger 3} S_- , \quad S_{13} = \alpha_{13} a_2^{\dagger 7} S_- . \quad (12)$$

This correlation operator S includes various multiphonon excitations to account for both the anharmonicity of each vibrational mode and the strong correlation between these two modes, which are induced by the spin fluctuation. After some straightforward, though tedious, calculations similar to those in the second-level approximation, a set of 13 nonlinear coupled algebraic equations of the parameters α_i's are obtained. As in the second-level approximation, one needs to resort to numerical methods to solve these equations. Then, these parameters α_i's will in turn give the ground-state energy $E_0 = 1 - \eta^2 + \eta\alpha_1$ of the system.

TABLE I. Ground-state energies obtained in different levels and the results of previous studies.

k^2	First level	Second level	Third level	Exact	Refs. 5 and 8	Ref. 9	Ref. 11	Ref. 12
0.25	0.7958	0.7777	0.7742	0.774	0.7766	0.7883	0.7877	0.7766
0.5	0.6320	0.5931	0.5806	0.578	0.5920	0.6155	0.6119	0.5877
0.75	0.4831	0.4284	0.4066	0.400	0.4308	0.4609	0.4522	0.4173
1	0.3417	0.2750	0.2453	0.233	0.2838	0.3168	0.3017	0.2586
2	−0.1926	−0.2877	−0.3343	−0.369	−0.2454	−0.2166	−0.2577	−0.3157
3	−0.7081	−0.8184	−0.8704	−0.919	−0.7494	−0.7281	−0.7886	−0.8466
5	−1.7228	−1.8506	−1.9051	−1.961	−1.7500	−1.7371	−1.8225	−1.8716
7	−2.7298	−2.8685	−2.9231	−2.976	−2.7500	−2.7409	−2.8418	−2.8833
10	−4.2355	−4.3852	−4.4391	−4.485	−4.2500	−4.2436	−4.3600	−4.3937
15	−6.7401	−6.9019	−6.9538	−6.991	−6.7500	−6.7458	−6.8780	−6.9042
20	−9.2425	−9.4124	−9.4623	−9.493	−9.2500	−9.2468	−9.3894	−9.4111
30	−14.2449	−14.4257	−14.4719	−14.496	−14.2500	−14.2479	−14.4035	−14.4202

In Table I the numerical results for the first three levels of the successive coupled-cluster approximation over the whole range of the coupling parameter are tabulated. For comparison, we also tabulate the ground-state energies evaluated by the other methods. It can be observed that although the coupled-cluster method is not a variational method and the estimates of the ground-state energy at each level of approximation are not necessarily upper bounds of the energy, the method does systematically improve its estimation of the energy as we go to higher and higher levels of approximation. In accordance with the numerical data, the convergence of our results is fairly rapid, especially for the weak- and strong-coupling cases. Since our choice of the starting state is dictated primarily by our desire to use a calculationally manageable starting state and may not be a good one at all, one may thus improve the convergence of the successive coupled-cluster approximation by using a better starting state. It is also clear that over the whole range of the coupling parameter, our results for the ground-state energy are not only in good agreement with the exact numerical diagonalization results, but they are also better than those from earlier analytical studies. Accordingly, the successive coupled-cluster approximation seems to be a practical tool for calculating the ground-state energy of a vibronic system since only the first few levels of approximation will be needed in actual practice.

In summary, we have applied the successive coupled-cluster approximation up to the third level to investigate the ground state of the linear E-e Jahn-Teller system. Taking into account both the anharmonicity of each vibrational mode and the strong correlation between these two modes, which are induced by the spin fluctuation, the coupled-cluster approximation provides a treatment better than previous analytical studies over the whole range of the coupling parameter. Its estimates of the ground-state energies are also in good agreement with the exact numerical results. Since the mathematical treatment in this work is quite simple and could be easily extended to the studies of the more complicated cases, we hope this method could be applied to the many-electron systems where the cooperative dynamical Jahn-Teller effect plays a major role.

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