Chapter 8

Application of the CCM to Linear $E \otimes e$ Jahn–Teller Systems

In this chapter, we review previous applications of the CCM to the ground state of the linear $E \otimes e$ JT Hamiltonian, and present new CCM results for the ground and first excited state energies of both the linear $E \otimes e$ JT and PJT models. Given the observed character change in the ground state of these models, it is not surprising to find that, as is the case for the Rabi Hamiltonian, a CCM calculation based on a naive choice of the model state fails in the intermediate coupling regime. We present, however, a CCM calculation, based on the analytic ground state of the linear $E \otimes e$ resonant pseudo Jahn–Teller (RPJT) Hamiltonian, which to first order yields excellent results for both the ground and first excited states of the models considered here.

8.1 Previous CCM calculations for the linear $E \otimes e$ Jahn–Teller Hamiltonian

Monkhorst presented a critical analysis of the treatment of molecular systems in the adiabatic approximation, and argued that the CCM is an especially suitable method for the analysis of such systems in a manner which does not rely on the adiabatic approximation [Mo87]. Wong and Lo have applied the CCM to the ground state of the linear $E \otimes e$ JT Hamiltonian, which is a manifestly non–adiabatic model. Initially, these authors applied the unitary transformation

$$U = \exp R, \quad R = \lambda \left(b_1^\dagger - b_1 \right) , \tag{8.1}$$

with $\lambda = \eta/\omega$, to the Hamiltonian in the form

$$H_{\rm JT} = \omega \left(b_1^\dagger b_1 + b_2^\dagger b_2 \right) + \eta \left(b_1^\dagger + b_1 \right) \sigma^x - \eta \left(b_2^\dagger + b_2 \right) \sigma^y , \tag{8.2}$$

and applied the CCM to the transformed Hamiltonian using the SCCA approximation scheme discussed in Section 5.1 [Wo94]. The same authors subsequently presented an improved ground–state CCM calculation for $H_{\rm JT}$, referred to as the optimal coupled cluster approximation [Wo96a]. In this approach, the parameter λ in the unitary transformation (8.1) is treated as a variational parameter, the optimal value λ^* of which is determined by a method which combines aspects of both the CCM and the variational method. Finally, the CCM is applied to the "optimally" ($\lambda = \lambda^*$) transformed Hamiltonian to yield the required ground–state energy results.

The optimal CCM results of Wong and Lo for the ground–state energy of $H_{\rm JT}$ are more accurate, over the full coupling spectrum, than those ob-

tained via previous calculations based on either the variational method or the method of unitary transformations [Wo96a]. Their calculations, however, take no account of either of the symmetries J and Π_{PJT} of the Hamiltonian; in fact, it is evident that the unitary transformation (8.1) destroys both these symmetries. Besides the resulting loss of accuracy in the ground–state energy results, their approach is therefore also not readily generalized either to the first excited state, or to the case of nondegenerate electronic levels ($\omega_0 > 0$).

8.2 Naive applications of the CCM to H_{JT} and H_{PJT}

We have generalized the CCM schemes [1] employed in our application of the method to the Rabi Hamiltonian (see Table D.1) to the linear $E \otimes e$ JT and PJT case of two degenerate bosonic modes. Given the results obtained for the Rabi Hamiltonian via CCM calculations based on the noninteracting model state, and the character change in the ground states of H_{JT} and H_{PJT}, it is unreasonable to expect that a CCM calculation based on the model state $|0\rangle|0\rangle|\downarrow\rangle$ would be successful here. Indeed, we have confirmed that, for the model state $|0\rangle|0\rangle|\downarrow\rangle$ and a cluster operator S of the form

$$S = \sum_{n=1}^{\infty}\sum_{k=0}^{n} s_{n,k}^{(1)} \left(b_1^\dagger\right)^k \left(b_2^\dagger\right)^{n-k} + \sum_{n=1}^{\infty}\sum_{k=0}^{n-1} s_{n,k}^{(2)} \left(b_1^\dagger\right)^k \left(b_2^\dagger\right)^{n-k-1} \sigma^+ , \quad (8.3)$$

which represents a simple generalization of Scheme I for the Rabi Hamiltonian, the CCM results, although very accurate for weak coupling, again fail

[1] As before, a CCM scheme refers to a particular choice of the model state $|\Phi\rangle$ and cluster operator S.

at intermediate and large coupling. The same holds true for the generalization of Scheme II. Although we have not formally proven this, it is highly likely that the failure of the method is again due to an incompleteness, to any finite order, in the CCM ansatz for the ground–state wave function. Also, these calculations do not conserve the J symmetry of the Hamiltonians $H_{\rm JT}$ and $H_{\rm PJT}$.

We have also performed a CCM calculation for $H_{\rm JT}$ and $H_{\rm PJT}$ based on a coupling–dependent model state of the form

$$|\Phi\rangle = \frac{1}{\sqrt{2}}\{|-x\rangle|0\rangle|\uparrow;\sigma^x\rangle - |x\rangle|0\rangle|\downarrow;\sigma^x\rangle\} \ . \tag{8.4}$$

Here $|x\rangle$ is a bosonic coherent state with coherent parameter $x = \eta/\omega$, the bosonic states refer to modes of linear polarization, and the fermionic states refer to eigenstates of σ^x. The state (8.4) represents a generalized form of the model state $|\Psi_+\rangle$ employed in the Scheme III analysis of the Rabi Hamiltonian. Using a similar form for the cluster operator S to that employed there, we again find that the CCM breaks down at intermediate and large coupling. The reason is two–fold: the model state (8.4) does not mimic the change in character in the ground states of $H_{\rm JT}$ and $H_{\rm PJT}$ with sufficient accuracy, and the J symmetry has again been neglected.

Since an accurate variational calculation similar to that presented in Chapter 4 for the Rabi Hamiltonian is not available for the linear $E \otimes e$ JT and PJT Hamiltonians, it is not possible to generalize the very successful CCM Scheme IV calculation for the Rabi Hamiltonian to the models considered here. For a CCM analysis of $H_{\rm JT}$ and $H_{\rm PJT}$, we therefore seek an alternative model state $|\Phi\rangle$ which must

- incorporate the symmetries Π_{PJT} and J,
- allow for the construction of a suitable cluster operator S which conserves these symmetries, and
- be capable of tracking the character change in the ground state.

8.3 Successful CCM calculations for H_{JT} and H_{PJT}

For the Hamiltonians H_{JT} and H_{PJT}, the analytic ground state of the linear $E \otimes e$ RPJT Hamiltonian, [2]

$$|\Psi_0^{\mathrm{RPJT}}\rangle = \frac{1}{\sqrt{I_0\left(2\kappa^2\right) + I_1\left(2\kappa^2\right)}} \left\{ I_0\left(2\kappa c^\dagger\right) - I_1\left(2\kappa c^\dagger\right) \right\} |0\rangle|0\rangle|\downarrow\rangle \qquad (8.5)$$

with $\kappa \equiv \gamma/\omega$, and where the operator $c^\dagger$ was introduced in (7.8), satisfies all the requirements for an effective CCM model state [Bi99b]. The state $|\Psi_0^{\mathrm{RPJT}}\rangle$ clearly has the correct even–parity and $j = -1/2$ symmetries required of the ground state. Furthermore, since it is easily shown that

$$c|\Psi_0^{\mathrm{RPJT}}\rangle = -\kappa|\Psi_0^{\mathrm{RPJT}}\rangle \,, \qquad (8.6)$$

the operator $c + \kappa$ annihilates the model state $|\Phi\rangle = |\Psi_0^{\mathrm{RPJT}}\rangle$. This suggests the following (clearly symmetry–conserving) form for the cluster correlation operator S:

$$S = \sum_{n=1}^{\infty} s_n \left(c^\dagger + \kappa\right)^n \,. \qquad (8.7)$$

We shall refer to this choice of the model state and correlation operator as the RPJT scheme. Consider the SUB-1 approximation, where $S = s_1\left(c^\dagger + \kappa\right)$.

[2] Here I_n refers to a modified Bessel function of the first kind of order n.

With the Hamiltonian $H_{\rm PJT}$ (for arbitrary ω_0 including the JT case $\omega_0 = 0$) written in the convenient form (7.11), the nested commutator expansion (3.8) may be used to obtain the similarity transformed Hamiltonian

$$\begin{aligned} e^{-S} H_{\rm PJT} e^{S} &= \frac{1}{2}\omega_0 \exp\left\{-2s_1 c^\dagger\right\}\sigma^z + 2\omega c^\dagger c - \frac{1}{2}\omega \\ &\quad + \omega s_1 \left(c^\dagger + \kappa\right) + 2\omega\kappa\left(c^\dagger + c\right) \\ &\quad + \frac{1}{2}\omega\,(2J)\,\sigma^z + \frac{1}{2}\omega \sum_{m=0}^{\infty} \frac{2s_1\kappa\left(-2s_1 c^\dagger\right)^m}{(m+1)!}\,(2J)\,\sigma^z . \end{aligned} \tag{8.8}$$

For the ground state, one may make the replacement $2J \to -1$. Furthermore, given the relation $c|\Phi\rangle = (-\kappa)|\Phi\rangle$ and its Hermitian conjugate $\langle\Phi|c^\dagger = \langle\Phi|(-\kappa)$, it follows that the SUB-1 CCM ground–state energy has the form

$$\begin{aligned} E_0^{\rm CCM} &= \langle\Phi|e^{-S} H_{\rm PJT} e^{S}|\Phi\rangle \\ &= -\frac{1}{2}\omega - 2\omega\kappa^2 + \frac{1}{2}\left(\omega_0 - \omega\right)\exp\left\{2s_1\kappa\right\}\langle\sigma^z\rangle \ , \end{aligned} \tag{8.9}$$

where the model state expectation value $\langle\sigma^z\rangle$ is given by

$$\langle\sigma^z\rangle = \langle\Phi|\sigma^z|\Phi\rangle = -\left[\frac{I_0\left(2\kappa^2\right) - I_1\left(2\kappa^2\right)}{I_0\left(2\kappa^2\right) + I_1\left(2\kappa^2\right)}\right] . \tag{8.10}$$

Using the commutation relations (7.13), one obtains the overlap equation

$$\begin{aligned} 0 &= \langle\Phi|\left(c + \kappa\right) e^{-S} H_{\rm PJT} e^{S}|\Phi\rangle \\ &= \exp\left\{2s_1\kappa\right\}\left(\omega_0 - \omega\right)\left(\kappa - \frac{1}{2}s_1\right)\langle\sigma^z\rangle + \frac{1}{2}\omega s_1\left[1 - \langle\sigma^z\rangle\right] \\ &\quad + \frac{\omega_0}{4\kappa}\sinh\left\{2s_1\kappa\right\} + \frac{\omega}{4\kappa}\left[1 - \cosh\left\{2s_1\kappa\right\}\right] \\ &\quad + \frac{\omega}{4\kappa}\left[1 - \exp\left\{2s_1\kappa\right\}\right]\langle\sigma^z\rangle \ , \end{aligned} \tag{8.11}$$

which determines the coefficient s_1, and thereby also the SUB-1 CCM ground–state energy (8.9) in the RPJT scheme. It is clear from the form (8.9) that, as expected, the SUB-1 CCM ground–state energy $E_0^{\rm CCM}$ for the RPJT scheme is exact in the case of resonance $\omega_0 = \omega$.

For ease of comparison with other results, we scale out the ω–dependence of the Hamiltonian by setting $\omega = 1$, and introduce the coupling parameter

$$k^2 \equiv 4\gamma^2 = 4\kappa^2 = 2\eta^2 \qquad (\omega = 1) \ . \tag{8.12}$$

In Table 8.1 we compare our SUB-1 CCM results for the ground–state energy of the (pure) linear $E \otimes e$ Hamiltonian (for which $\omega_0 = 0$) to the numerically exact results obtained via the CI diagonalization, and also to results obtained

Table 8.1: *Comparison of the ground–state energy $E_0^{\rm CCM}$ of the scaled ($\omega = 1$) linear $E \otimes e$ JT ($\omega_0 = 0$) Hamiltonian, obtained as a function of the coupling k^2 from a SUB-1 CCM calculation based on the RPJT scheme, with the results of other many–body calculations. In accordance with the other results quoted here, we have added unity (the zero–point energy of the bosonic modes for $\omega = 1$) to our results. The (effectively exact) CI results are labeled $E_0^{\rm CI}$. The results from [Wo96a] are the so–called optimal CCM ground–state energy results obtained there. The other columns, which are reproduced from [Wo96a], represent results obtained via an earlier CCM analysis [Wo94], and via variational methods and the method of unitary transformations [Al69, Ba78, Ba77, Zh90, Lo91].*

k^2	$E_0^{\rm CI}+1$	$E_0^{\rm CCM}+1$	[Wo96a]	[Wo94]	[Al69, Ba78]	[Ba77]	[Zh90]	[Lo91]
0.00	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
0.25	0.7738	0.7739	0.7741	0.7742	0.7766	0.7883	0.7877	0.7767
0.50	0.5780	0.5785	0.5799	0.5806	0.5920	0.6155	0.6119	0.5877
0.75	0.3997	0.4009	0.4045	0.4066	0.4308	0.4609	0.4522	0.4173
1.00	0.2330	0.2350	0.2415	0.2453	0.2838	0.3168	0.3017	0.2586
2.00	-0.3689	-0.3637	-0.3441	-0.3343	-0.2454	-0.2166	-0.2577	-0.3157
3.00	-0.9189	-0.9117	-0.8824	-0.8704	-0.7494	-0.7281	-0.7886	-0.8466
5.00	-1.9610	-1.9532	-1.9173	-1.9051	-1.9750	-1.7371	-1.8225	-1.8716
7.00	-2.9761	-2.9693	-2.9345	-2.9231	-2.7500	-2.7409	-2.8418	-2.8833
10.00	-4.4850	-4.4797	-4.4492	-4.4391	-4.2500	-4.4360	-4.3600	-4.3937
15.00	-6.9907	-6.9870	-6.9625	-6.9538	-6.7500	-6.7458	-6.8780	-6.9042
20.00	-9.4932	-9.4904	-9.4700	-9.4623	-9.2500	-9.2468	-9.3894	-9.4111
30.00	-14.4956	-14.4937	-14.4783	-14.4719	-14.2500	-14.2479	-14.4035	-14.4202

via a variety of many–body calculations. It is clear that, even in first order, our CCM calculation based on the RPJT scheme yields a considerable improvement, over the full coupling spectrum, on the earlier "optimal" CCM results of [Wo96a], which in turn are far superior to results obtained via other many–body techniques. Furthermore, the CCM results of Wong and Lo given in [Wo96a] were obtained in the third level of their successive coupled cluster approximation scheme, and required the numerical solution of 13 nonlinear coupled equations. It is evident that the proper inclusion of the J and $\Pi_{\rm PJT}$ symmetries in our calculation, which requires the numerical solution of only the single trancendental equation (8.11), leads to a much simpler and considerably more accurate CCM calculation of the linear $E \otimes e$ JT ground–state energy.

In Table 8.2 we present the results of a SUB-1 CCM calculation, based on the RPJT scheme, of the ground–state energy of the scaled ($\omega = 1$) linear $E \otimes e$ PJT Hamiltonian in the sub–resonant cases $\omega_0 = 0$ (this is again the pure JT case) and $\omega_0 = 0.5$, as a function of the coupling k^2. Here we also show the percentage error in the CCM results, as compared to the (converged) results of a CI diagonalization of $H_{\rm PJT}$ in a basis consisting of 101 even–parity $j = -1/2$ states. Similar results for the supra–resonant cases $\omega_0 = 1.5$ and $\omega_0 = 2.0$ are tabulated in Table 8.3. It is clear that, already in the SUB-1 approximation, the CCM ground–state energy results for the RPJT scheme are extremely accurate over the full coupling regime and for a wide range of values of the fermionic level splitting ω_0, with a percentage error, relative to the CI results, of no more than 0.38 % (see Figure 8.1) for the range of parameters considered here.

Table 8.2: *The ground-state energy* E_0^{CCM} *of the scaled* ($\omega = 1$) *linear* $E \otimes e$ *PJT Hamiltonian, in the sub-resonant cases* $\omega_0 = 0.0$ *and* $\omega_0 = 0.5$, *obtained as a function of the coupling* k^2 *from a SUB-1 CCM calculation based on the RPJT scheme, compared to results (labeled* E_0^{CI}) *obtained via a CI diagonalization. Also shown is the percentage error* $\left|E_0^{\mathrm{CCM}} - E_0^{\mathrm{CI}}\right| / E_0^{\mathrm{CI}} \times 100$.

ω_0	k^2	E_0^{CI}	E_0^{CCM}	% Error
0.0	0.00	0.0000	0.0000	0.00
	0.25	-0.2262	-0.2261	0.04
	0.50	-0.4220	-0.4215	0.12
	0.75	-0.6003	-0.5991	0.20
	1.00	-0.7670	-0.7650	0.26
	2.00	-1.3689	-1.3637	0.38
	3.00	-1.9189	-1.9117	0.38
	5.00	-2.9610	-2.9532	0.26
	7.00	-3.9761	-3.9693	0.17
	10.00	-5.4850	-5.4797	0.10
	15.00	-7.9907	-7.9870	0.05
	20.00	-10.4932	-10.4904	0.03
	30.00	-15.4956	-15.4937	0.01
0.5	0.00	-0.2500	-0.2500	0.00
	0.25	-0.4125	-0.4125	0.00
	0.50	-0.5679	-0.5679	0.00
	0.75	-0.7180	-0.7178	0.03
	1.00	-0.8639	-0.8635	0.05
	2.00	-1.4191	-1.4179	0.08
	3.00	-1.9481	-1.9463	0.09
	5.00	-2.9736	-2.9716	0.07
	7.00	-3.9832	-3.9815	0.04
	10.00	-5.4892	-5.4878	0.03
	15.00	-7.9932	-7.9922	0.01
	20.00	-10.4950	-10.4943	0.01
	30.00	-15.4967	-15.4963	0.00

Table 8.3: *The ground–state energy* E_0^{CCM} *of the scaled* $(\omega = 1)$ *linear* $E \otimes e$ *PJT Hamiltonian, in the supra–resonant cases* $\omega_0 = 1.5$ *and* $\omega_0 = 2.0$*, obtained as a function of the coupling* k^2 *from a SUB-1 CCM calculation based on the RPJT scheme, compared to results (labeled* E_0^{CI}*) obtained via a CI diagonalization. Also shown is the percentage error* $\left|E_0^{\mathrm{CCM}} - E_0^{\mathrm{CI}}\right| / E_0^{\mathrm{CI}} \times 100$.

ω_0	k^2	E_0^{CI}	E_0^{CCM}	% Error
1.5	0.00	-0.7500	-0.7500	0.00
	0.25	-0.8510	-0.8510	0.00
	0.50	-0.9540	-0.9539	0.01
	0.75	-1.0589	-1.0588	0.01
	1.00	-1.1656	-1.1654	0.02
	2.00	-1.6095	-1.6085	0.06
	3.00	-2.0745	-2.0728	0.08
	5.00	-3.0402	-3.0382	0.07
	7.00	-4.0264	-4.0245	0.05
	10.00	-5.5174	-5.5159	0.03
	15.00	-8.0111	-8.0101	0.01
	20.00	-10.5082	-10.5074	0.01
	30.00	-15.5054	-15.5048	0.00
2.0	0.00	-1.0000	-1.0000	0.00
	0.25	-1.0845	-1.0845	0.00
	0.50	-1.1714	-1.1713	0.01
	0.75	-1.2607	-1.2604	0.02
	1.00	-1.3525	-1.3519	0.04
	2.00	-1.7440	-1.7407	0.19
	3.00	-2.1708	-2.1645	0.29
	5.00	-3.0945	-3.0861	0.27
	7.00	-4.0625	-4.0549	0.19
	10.00	-5.5413	-5.5354	0.11
	15.00	-8.0266	-8.0224	0.05
	20.00	-10.5196	-10.5164	0.03
	30.00	-15.5129	-15.5107	0.01

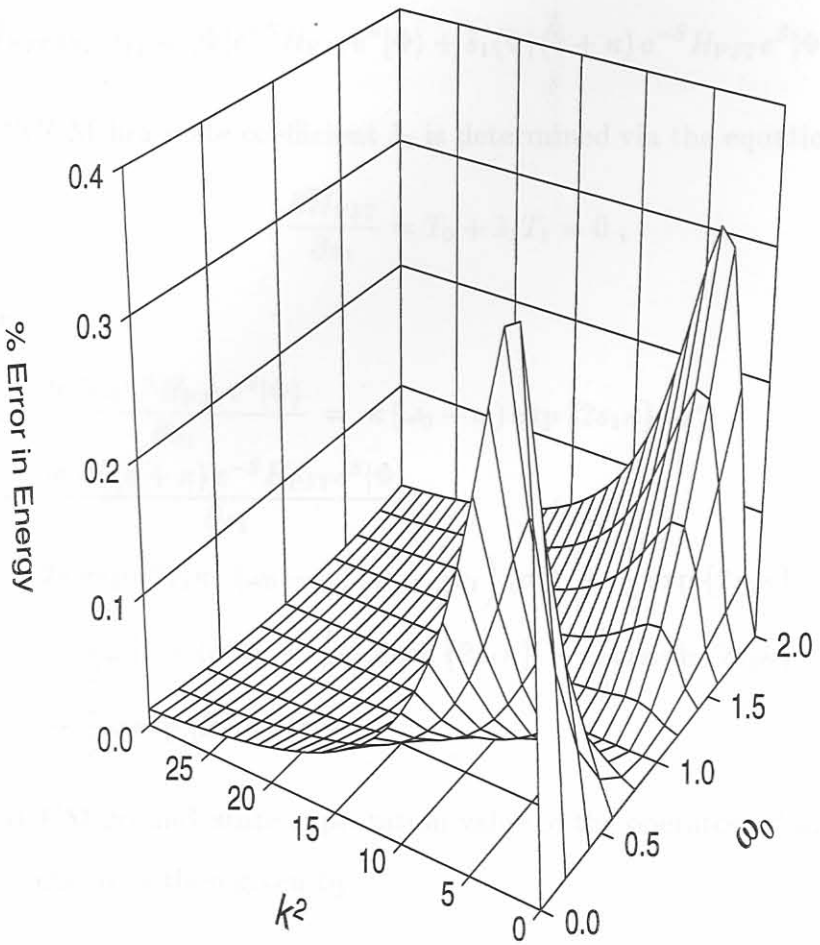


Figure 8.1: *The percentage error, as compared to the results of a CI diagonalization, in the ground–state energy of the scaled* ($\omega = 1$) *linear* $E \otimes e$ *PJT Hamiltonian obtained from a SUB-1 CCM calculation based on the RPJT scheme, as a function of the coupling* k^2 *and the two–level splitting* ω_0.

In order to determine ground–state expectation values other than the energy in the SUB-1 RPJT scheme, we construct the energy functional

$$\overline{H}_{\rm PJT}\left[s_1,\tilde{s}_1\right] = \langle\Phi|e^{-S}H_{\rm PJT}e^{S}|\Phi\rangle + \tilde{s}_1\langle\Phi|\left(c+\kappa\right)e^{-S}H_{\rm PJT}e^{S}|\Phi\rangle\ . \qquad (8.13)$$

The NCCM bra state coefficient $\tilde{s}_1$ is determined via the equation

$$\frac{\partial\overline{H}_{\rm PJT}}{\partial s_1} = T_0 + \tilde{s}_1 T_1 = 0\ , \qquad (8.14)$$

where

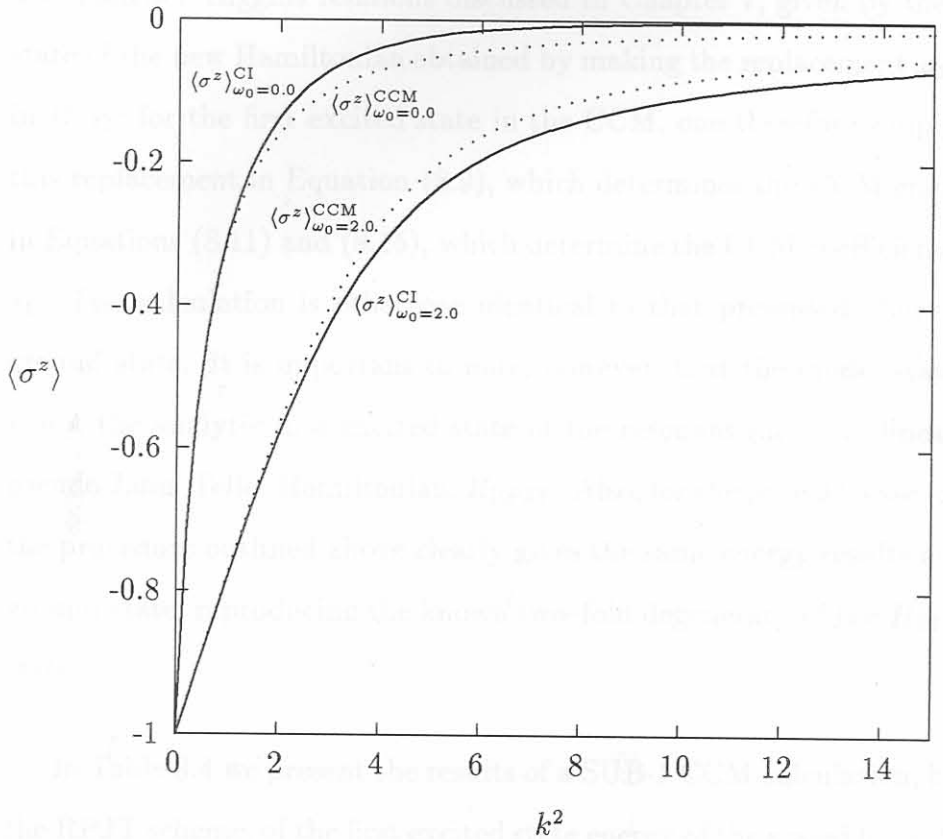
$$\begin{aligned}
T_0 &\equiv \frac{\partial\langle\Phi|e^{-S}H_{\rm PJT}e^{S}|\Phi\rangle}{\partial s_1} = \kappa\left(\omega_0-\omega\right)\exp\left\{2s_1\kappa\right\}\langle\sigma^z\rangle \\
T_1 &\equiv \frac{\partial\langle\Phi|\left(c+\kappa\right)e^{-S}H_{\rm PJT}e^{S}|\Phi\rangle}{\partial s_1} \\
&= 2\kappa\exp\left\{2s_1\kappa\right\}\left(\omega_0-\omega\right)\left(\kappa-\frac{1}{2}s_1\right)\langle\sigma^z\rangle + \frac{1}{2}\exp\left\{2s_1\kappa\right\}\left(\omega_0-\omega\right)\langle\sigma^z\rangle \\
&\quad + \frac{1}{2}\omega\left[1-\langle\sigma^z\rangle\right] + \frac{1}{2}\omega_0\cosh\left\{2s_1\kappa\right\} - \frac{1}{2}\omega\sinh\left\{2s_1\kappa\right\} \\
&\quad - \frac{1}{2}\omega\exp\left\{2s_1\kappa\right\}\langle\sigma^z\rangle\ . \qquad (8.15)
\end{aligned}$$

The NCCM ground–state expectation value of the operator σ^z in the SUB-1 RPJT scheme is then given by

$$\langle\sigma^z\rangle^{\rm CCM} = \exp\left\{2s_1\kappa\right\}\langle\sigma^z\rangle\left(1-s_1\tilde{s}_1+2\kappa\tilde{s}_1\right) + \frac{\tilde{s}_1}{2\kappa}\sinh\left\{2s_1\kappa\right\}\ , \qquad (8.16)$$

with s_1 and $\tilde{s}_1$ determined via (8.11) and (8.15), respectively. In Figure 8.2, our results for $\langle\sigma^z\rangle^{\rm CCM}$, for the representative cases $\omega_0 = 0$ and $\omega_0 = 2.0$, are compared to the numerical diagonalization results. Our CCM results, though quantitatively inaccurate for intermediate and large coupling, are at least qualitatively acceptable over the full coupling spectrum.

Figure 8.2: *The ground–state expectation value* $\langle\sigma^z\rangle$ *for the scaled* ($\omega = 1$) *linear* $E \otimes e$ *PJT Hamiltonian, in the representative cases* $\omega_0 = 0.0$ *and* $\omega_0 = 2.0$, *obtained as a function of the coupling* k^2 *from a SUB-1 CCM calculation based on the RPJT scheme (dotted lines labeled* $\langle\sigma^z\rangle^{\rm CCM}$*), compared to results obtained via a CI diagonalization (solid lines labeled* $\langle\sigma^z\rangle^{\rm CI}$*).*



The first excited state energy of $H_{\rm PJT}$ is useful in *e.g.* the analysis of the optical absorption properties of the linear $E \otimes e$ PJT model. Since the symmetries of the Hamiltonian $H_{\rm PJT}$ are built into our calculation, it is straightforward to extend the CCM analysis based on the RPJT scheme to the first excited state of $H_{\rm PJT}$, which is an odd–parity state corresponding to $j = 1/2$. This can be done by repeating the ground–state analysis above,

but with a model state of the form

$$|\Phi\rangle = \frac{1}{\sqrt{I_0\left(2\kappa^2\right) + I_1\left(2\kappa^2\right)}} \left\{ I_0\left(2\kappa c^\dagger\right) - I_1\left(2\kappa c^\dagger\right) \right\} |0\rangle|0\rangle|\uparrow\rangle \,. \qquad (8.17)$$

However, it is easily shown that this is equivalent to the following procedure: the first excited state of $H_{\rm PJT}$ is, due to the invariance properties of the (exact) Longuet–Higgins relations discussed in Chapter 7, given by the ground state of the new Hamiltonian obtained by making the replacement $\omega_0 \rightarrow -\omega_0$ in $H_{\rm PJT}$; for the first excited state in the CCM, one therefore simply makes this replacement in Equation (8.9), which determines the CCM energy, and in Equations (8.11) and (8.15), which determine the CCM coefficients s_1 and $\tilde{s}_1$. The calculation is otherwise identical to that presented above for the ground state. It is important to note, however, that the model state (8.17) is not the analytic first excited state of the resonant ($\omega_0 = \omega$) linear $E \otimes e$ pseudo Jahn–Teller Hamiltonian, $H_{\rm RPJT}$. Also, for the pure JT case ($\omega_0 = 0$), the procedure outlined above clearly gives the same energy results as for the ground state, reproducing the known two–fold degeneracy of the $H_{\rm JT}$ ground state.

In Table 8.4 we present the results of a SUB-1 CCM calculation, based on the RPJT scheme, of the first excited state energy of the scaled ($\omega = 1$) linear $E \otimes e$ PJT Hamiltonian, in the cases $\omega_0 = 0.5$ and $\omega_0 = 1.0$, as a function of the coupling k^2. We also show the percentage error in the CCM results, as compared to the (converged) results of a CI diagonalization of $H_{\rm PJT}$ in a basis consisting of 101 odd–parity $j = 1/2$ states. Though not as good as the ground–state results, the CCM results for the first excited state energy are still very accurate, over the full coupling spectrum, for the range of ω_0

Table 8.4: *The first excited state energy* E_1^{CCM} *of the scaled* $(\omega = 1)$ *linear* $E \otimes e$ *PJT Hamiltonian, in the cases* $\omega_0 = 0.5$ *and* $\omega_0 = 1.0$, *obtained as a function of the coupling* k^2 *from a SUB-1 CCM calculation based on the RPJT scheme, compared to results (labeled* E_1^{CI}*) obtained via a CI diagonalization. Also shown is the percentage error* $\left|E_1^{\mathrm{CCM}} - E_1^{\mathrm{CI}}\right| / E_1^{\mathrm{CI}} \times 100$.

ω_0	k^2	E_1^{CI}	E_1^{CCM}	% Error
0.5	0.00	0.2500	0.2500	0.000000
	0.25	-0.0935	-0.0930	0.531421
	0.50	-0.3325	-0.3307	0.528784
	0.75	-0.5351	-0.5317	0.636452
	1.00	-0.7176	-0.7124	0.726559
	2.00	-1.3505	-1.3387	0.874016
	3.00	-1.9123	-1.8967	0.815322
	5.00	-2.9620	-2.9454	0.559254
	7.00	-3.9785	-3.9641	0.361388
	10.00	-5.4874	-5.4763	0.201573
	15.00	-7.9925	-7.9848	0.096169
	20.00	-10.4946	-10.4888	0.055698
	30.00	-15.4966	-15.4927	0.025425
1.0	0.00	0.5000	0.5000	0.000000
	0.25	-0.0560	-0.0558	0.395322
	0.50	-0.3173	-0.3156	0.552823
	0.75	-0.5307	-0.5267	0.757497
	1.00	-0.7197	-0.7130	0.921794
	2.00	-1.3633	-1.3466	1.227422
	3.00	-1.9277	-1.9047	1.192903
	5.00	-2.9764	-2.9511	0.848603
	7.00	-3.9904	-3.9682	0.554943
	10.00	-5.4963	-5.4792	0.310645
	15.00	-7.9986	-7.9868	0.148102
	20.00	-10.4993	-10.4903	0.085685
	30.00	-15.4997	-15.4936	0.039062

considered here. For $\omega_0 > 1$, the SUB-1 calculation based on the RPJT scheme breaks down, indicating that the model state (8.17) is not a physically realistic starting state for the first excited state beyond $\omega_0 = 1$.

In Figure 8.3 we plot the percentage error in the results of the SUB-1 RPJT scheme calculation of the first excited state energy of H_{PJT}, as compared to results obtained via the CI method, as a function of k^2 and ω_0. For the range $0 \leq \omega_0 \leq 1$, the maximum percentage error of 1.2 % occurs at intermediate coupling for the resonant case $\omega_0 = 1$. Thus we have shown that, even to first order, the CCM can yield very accurate results for the ground and first excited states of the linear $E \otimes e$ JT and PJT Hamiltonians, provided that a model state is chosen which not only mimics the physical behaviour of these states, but also incorporates the correct J and Π_{PJT} symmetries.

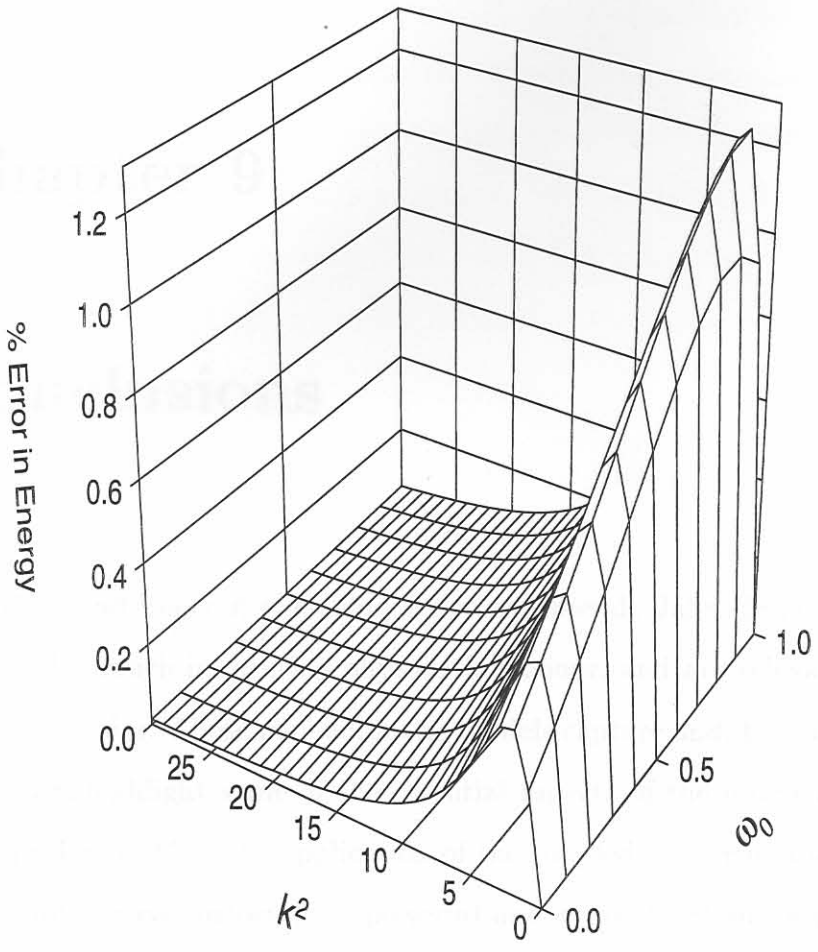


Figure 8.3: *The percentage error, as compared to the results of a CI diagonalization, in the first excited state energy of the scaled* ($\omega = 1$) *linear* $E \otimes e$ *PJT Hamiltonian obtained from a SUB-1 CCM calculation based on the RPJT scheme, as a function of the coupling* k^2 *and the two–level splitting* ω_0.