



# Coupled cluster analysis of model non-adiabatic Hamiltonians

Coupled cluster analysis of model  
non-adiabatic Hamiltonians

by

David Michael van der Walt

Philosophiae Doctor (Physics)  
in the Faculty of Science

University of Pretoria

Pretoria

April 1999

Supervisor: Prof. R. M. Carter

Co-supervisor: Dr N. J. Davidson

In this thesis we undertake a theoretical many-body investigation into the

Submitted in partial fulfillment of the requirements for the degree

describing the interaction of a few particles with one or more

modes of a quantised bosonic field. These models are of topical interest in

quantum optics, solid state physics and quantum chemistry, and we focus

here in particular on the Jahn-Hamiltonian for Jahn-Teller systems

without the rotating wave approximation in quantum optics, and the  $E \otimes e$  Jahn-Teller and pseudo Jahn-Teller systems in quantum chemistry.

Due to their simplicity, these Hamiltonians exhibit interesting symmetries,

allowing them to serve as useful testing grounds for quantum many-

# Abstract

## **Coupled cluster analysis of model non-adiabatic Hamiltonians**

by

**David Michael van der Walt**

Submitted in partial fulfillment of the requirements for the degree

**Philosophiae Doctor (Physics)**

in the Faculty of Science

University of Pretoria

Pretoria

April 1999

Supervisor: Prof. R. M. Carter

Co-supervisor: Dr N. J. Davidson

In this thesis, we undertake a theoretical many-body investigation into the ground and first excited states of a class of model non-adiabatic Hamiltonians describing the interaction of a two-level fermionic system with one or more modes of a quantized bosonic field. These models are of topical interest in quantum optics, solid state physics and quantum chemistry, and we focus here in particular on the Rabi Hamiltonian (or Jaynes-Cummings model without the rotating wave approximation) in quantum optics, and the linear  $E \otimes e$  Jahn-Teller and pseudo Jahn-Teller systems in quantum chemistry.

Due to their simplicity, these Hamiltonians exhibit interesting symmetries, allowing them to serve as useful testing grounds for quantum many-

body techniques. Here we analyze these models by means of the the coupled cluster method (CCM). The CCM has an impressive record as a powerful and versatile *ab initio* method, having been successfully applied in nuclear physics, quantum chemistry, lattice gauge and continuum field theories, and spin and electron lattice models. For comparison, we also present results for our model Hamiltonians obtained via a variety of other many-body methods. In particular, we present an excellent variational calculation for the Rabi Hamiltonian in which the importance of the incorporation of the correct symmetry in the variational ansatz is highlighted, as well as an elegant operator method useful in the analysis of the linear  $E \otimes e$  Jahn–Teller and pseudo Jahn–Teller models.

The CCM analysis of the class of Hamiltonians considered here displays a critical dependence on the choice of the model state and corresponding creation operators which characterize the method. For certain physically reasonable choices, we present a formal demonstration of an essential incompleteness, to any finite order, in the CCM ansatz for the ground-state wave function of the system. As a result, the CCM results for these systems strongly suggest a phase transition which does not in fact exist. We also show that, for certain other choices of the model state and creation operators, the CCM breaks down as a result of the non-Hermiticity of the method.

This breakdown of the CCM is closely related to the marked change in character of the ground state of the systems considered here. Using a model state which mimics this change in character, excellent CCM results for these systems can be obtained; in particular, we present a simple yet extremely accurate CCM calculation for the linear  $E \otimes e$  Jahn–Teller and pseudo Jahn–

Teller models. The dependence of the CCM results for the Hamiltonians considered here on the choice of the model state and creation operators is of considerable importance, given that the CCM formalism does not *a priori* specify this choice beyond the overall symmetry requirements of the Hamiltonian. The results demonstrate that the gross physical properties of the exact solution need to be reproduced by the model state if even qualitatively correct behaviour is to be obtained from a CCM calculation.

Voortreke van die natuurlike verdeling van die verskeie in die natuur

Philosophiese Doctor (Taal)

in die Fakulteit Natuurwetenskappe

Universiteit van Pretoria

Pretoria

April 1999

Promotor: Prof. J. M. Carter

Medepromotor: Dr. N. J. Davidson

In hierdie tesis word 'n verskeie verskeie wondersake gekyk na die natuur  
toestand en die ligte-ongewerkte toestand van 'n bepaalde klas van Hamilton  
niedel-Hamilton operatore wat die laterske-stryklyk tussen 'n Hamilton  
formalisme en 'n of meer model van 'n gekwanteerde toestand is.  
Hierdie modelle is teen verskeie belang in kwantumoptika, vastestof fisika en  
en kwantumchemie, en ons fokus hier spesifiek op die Heilm Hamilton-ope-  
rator (of Jaynes-Cummings model) watter die interaksie-woord betrekking is  
kwantumoptika, en die hierdie E- & Z- Jahn-Teller en kwant- Jahn-Teller  
toes in kwantumchemie.

As gevolg van hul eenvoud vertoon hierdie Hamilton operatore natuur

# Samevatting

## Gekoppelde–bondel–analise van model nie–adiabatiese Hamilton operatore

deur

David Michael van der Walt

Voorgelê ter gedeeltelike vervulling van die vereistes vir die graad

**Philosophiae Doctor (Fisika)**

in die Fakulteit Natuurwetenskappe

Universiteit van Pretoria

Pretoria

April 1999

Promotor: Prof. R. M. Carter

Medepromotor: Dr. N. J. Davidson

In hierdie tesis word 'n teoretiese veeldeeltjie–ondersoek geloods na die grondtoestand en die laagste opgewekte toestand van 'n bepaalde klas nie–adiabatiese model–Hamilton operatore wat die interaksie beskryf tussen 'n tweevlak fermionsisteem en een of meer modes van 'n gekwantiseerde bosoniese veld. Hierdie modelle is tans van belang in kwantumoptika, vastetoestandfisika en kwantumchemie, en ons fokus hier spesifiek op die Rabi Hamilton operator (of Jaynes–Cummings model sonder die roterende–golf–benadering) in kwantumoptika, en die lineêre  $E \otimes e$  Jahn–Teller en kwasi–Jahn–Teller sisteme in kwantumchemie.

As gevolg van hul eenvoud vertoon hierdie Hamilton operatore interes-

sante simmetrieë, wat hul in staat stel om as 'n toetsterrein te dien vir veeldeeltjietegnieke. Ons analiseer hierdie modelle hier deur middel van die gekoppelde-bondel-tegniek (CCM). Die CCM het 'n indrukwekkende rekord, en is al suksesvol aangewend in kernfisika, kwantumchemie, rooster-yk- en kontinuumveldteorië, en spin- en elektron-matriksmodelle. Ter vergelyking wys ons ook resultate vir ons model-Hamilton operatore wat deur middel van 'n verskeidenheid ander metodes verkry is. In die besonder bied ons 'n akkurate variasie berekening vir die Rabi Hamilton operator aan wat die belang van die insluiting van die korrekte simmetrieë in die variasie aanname beklemtoon, asook 'n elegante operatormetode wat in die analise van die lineêre  $E \otimes e$  Jahn-Teller en kwasi-Jahn-Teller sisteme benut kan word.

Die CCM analise van die klas Hamilton operatore wat hier beskou word toon 'n kritiese afhanklikheid van die keuse van modeltoestand en ooreenstemmende skeppingsoperatore wat die metode karakteriseer. Vir bepaalde fisies verantwoordbare keuses, toon ons formeel aan dat daar 'n essentiële ontoereikendheid bestaan, tot enige eindige orde, in die CCM-aanname vir die grondtoestand-golffunksie van die sisteem. As gevolg hiervan bied die CCM resultate sterk getuienis vir 'n fase-oorgang wat in werklikheid nie bestaan nie. Ons toon ook aan dat die CCM, vir sekere ander keuses van die modeltoestand en skeppingsoperatore, faal as gevolg van die nie-Hermitiese aard van die metode.

Hierdie mislukkings van die CCM is nou verwant aan die skerp gedragsverandering in die grondtoestand van die sisteme wat ons hier beskou. Mits 'n modeltoestand gebruik word wat hierdie gedragsverandering naboots, kan uitstekende CCM resultate vir hierdie sisteme verkry word; ons vertoon in

besonder 'n eenvoudige dog uiters akkurate CCM berekening vir die lineêre  $E \otimes e$  Jahn-Teller en kwasi-Jahn-Teller sisteme. Die modeltoestand- en skeppingsoperatorafhanklikheid van die CCM resultate vir die Hamilton operatore wat hier beskou word is van groot belang, gegewe dat die CCM nie *a priori* die keuse van of die modeltoestand of skeppingsoperatore voorskryf buiten die oorkoepelende simmetrieë van die Hamilton operator nie. Die resultate demonstreer dat die uitstaande fisieke eienskappe van die eksakte oplossing in die modeltoestand vervat moet word indien selfs kwalitatief korrekte gedrag deur middel van 'n CCM berekening verlang word.

# Acknowledgements

I would like to thank the following persons and institutions for their assistance in the preparation and completion of this thesis:

My supervisors, Prof. Rachel Carter and Dr Neil Davidson, for continued guidance, support and encouragement. I could not have asked for two better supervisors.

Prof. Ray Bishop at UMIST, UK, for useful guidance and discussion.

Hermann Uys, at the time an undergraduate student at the University of Pretoria, for his assistance with the numerical work on the strong-coupling perturbative approach to the Rabi Hamiltonian.

The Foundation for Research Development, the University of Pretoria, and Vista University, for financial assistance.

The secretaries of the Physics Department at the University of Pretoria, Mrs. A. Schickerling and Mrs. C. J. Vos, for their friendly assistance on numerous occasions.

Prof. D. J. Brink, University of Pretoria, for proofreading the manuscript.

Dr Glyn Jones, for proofreading the manuscript, and for providing much support and encouragement.

Finally, my wife Lynnette and son Michael, for continued support and encouragement, and for patiently doing without a husband and father, respectively, whenever I was “working on my PhD”.



5	Simple Applications of the CCM to the Rabi Hamiltonian	51
5.1	Earlier CCM analyses of the Rabi Hamiltonian	51
5.2	Evidence for a spurious symmetry-breaking phase transition	63
5.3	Incompleteness of the CCM ground-state ansatz	70

# Contents

6	Successful Application of the CCM to the Rabi Hamiltonian	77
1	<b>Introduction</b>	<b>1</b>
2	<b>The Model Hamiltonians</b>	<b>9</b>
2.1	The general model Hamiltonian	9
2.2	Special cases of the general Hamiltonian	11
2.2.1	The Rabi Hamiltonian	11
2.2.2	The linear $E \otimes e$ Jahn–Teller and pseudo Jahn–Teller Hamiltonians	12
3	<b>The Coupled Cluster Method</b>	<b>15</b>
4	<b>The Rabi Hamiltonian</b>	<b>23</b>
4.1	Discussion of the Rabi Hamiltonian	23
4.1.1	Exact limits of the Hamiltonian	26
4.1.2	Juddian solutions and the configuration–interaction (CI) method	29
4.2	Physical characteristics of the Rabi ground state	34
4.3	Approximate many–body approaches to the Rabi Hamiltonian	38
4.3.1	Time–independent perturbation theory	38
4.3.2	Variational results for the Rabi Hamiltonian	43

<b>5</b>	<b>Simple Applications of the CCM to the Rabi Hamiltonian</b>	<b>61</b>
5.1	Earlier CCM analyses of the Rabi Hamiltonian . . . . .	62
5.2	Evidence for a spurious symmetry-breaking phase transition .	63
5.3	Incompleteness of the CCM ground-state ansatz . . . . .	72
5.4	An alternative CCM calculation based on the noninteracting model state . . . . .	76
<b>6</b>	<b>Successful Application of the CCM to the Rabi Hamiltonian</b>	<b>78</b>
6.1	Coupling-dependent CCM model states for the Rabi Hamil- tonian . . . . .	79
6.2	The method of unitary transformations . . . . .	85
<b>7</b>	<b>The Linear <math>E \otimes e</math> Jahn-Teller and Pseudo Jahn-Teller Hamil- tonians</b>	<b>88</b>
7.1	Discussion of the Hamiltonians . . . . .	89
7.1.1	Vibronic interactions and non-adiabaticity in quantum chemistry . . . . .	90
7.1.2	Analytic solutions in the limit of zero coupling . . . . .	93
7.1.3	Numerical diagonalization of the JT and PJT models .	94
7.1.4	Juddian solutions for the JT and PJT models . . . . .	100
7.2	Physical characteristics of the JT and PJT ground states . . .	105
7.3	Approximate many-body approaches to the JT and PJT models	107
<b>8</b>	<b>Application of the CCM to Linear <math>E \otimes e</math> Jahn-Teller Systems</b>	<b>109</b>
8.1	Previous CCM calculations for the linear $E \otimes e$ Jahn-Teller Hamiltonian . . . . .	110
8.2	Naive applications of the CCM to $H_{JT}$ and $H_{PJT}$ . . . . .	111

8.3	Successful CCM calculations for $H_{JT}$ and $H_{PJT}$ . . . . .	113
<b>9</b>	<b>Conclusions</b>	<b>126</b>
<b>A</b>	<b>Derivation of the General Model Hamiltonian</b>	<b>132</b>
A.1	The two-level atom . . . . .	132
A.2	Quantization of the electromagnetic field . . . . .	133
A.3	The dipole interaction Hamiltonian . . . . .	135
<b>B</b>	<b>Useful Identities and Commutation Relations</b>	<b>138</b>
B.1	Operators for two-level systems . . . . .	139
B.2	General commutation relations . . . . .	140
B.2.1	The Hausdorff expansion . . . . .	141
B.2.2	Operators for which the commutator is a number . . .	142
B.3	Bosonic commutation relations . . . . .	143
<b>C</b>	<b>Explicit Forms for Variational Expressions</b>	<b>145</b>
C.1	The mixed-parity two-parameter ansatz (4.30) . . . . .	146
C.2	The good-parity two-parameter ansatz (4.38) . . . . .	147
C.3	The good-parity three-parameter ansatz (4.41) . . . . .	148
<b>D</b>	<b>Explicit Forms for CCM Expressions</b>	<b>153</b>
D.1	NCCM Scheme I . . . . .	156
D.1.1	Termination of the even-parity NCCM Scheme I calculation . . . . .	158
D.2	ECCM Scheme I . . . . .	160
D.2.1	The SUB-1 case . . . . .	162
D.3	NCCM Scheme II . . . . .	162

D.3.1	Analytics for the SUB-1 and SUB-2 cases . . . . .	163
D.4	NCCM Scheme III . . . . .	164
D.5	NCCM Scheme IV . . . . .	165

## E Acronyms and Abbreviations

170

### List of Figures

1.1	The expectation value $\langle n^2 \rangle$ and the fluctuation $\Delta n^2$ in the ground state of the resonant Rabi Hamiltonian as a function of the coupling $g$ .
1.2	The ground state energy $E_0$ of the resonant Rabi Hamiltonian as a function of the coupling $g$ , as determined via various numerical approaches. Inset: A zoomed-in view of the ground state energy $E_0$ for small values of the coupling $g$ .
1.3	The expectation value $\langle n^2 \rangle$ and the fluctuation $\Delta n^2$ in the even parity $\psi_{\pm}^{\pm}$ ground state $ \psi_{\pm}^{\pm}\rangle$ of the resonant Rabi Hamiltonian as a function of the coupling $g$ .
1.4	The ground state energy $E_0$ of the resonant Rabi Hamiltonian as a function of the coupling $g$ , as determined via a numerical calculation based on a mixed parity two-parameter ground state, and via an even-parity projection after variation of $\lambda$ based on the same state.
1.5	The expectation value $\langle n^2 \rangle$ in the ground state of the resonant Rabi Hamiltonian, as determined via various numerical calculations, as a function of the coupling $g$ .

## List of Figures

- 4.1 The expectation value  $\langle \sigma^z \rangle$  and the fluctuation  $\Delta \sigma^z$  in the ground state of the resonant Rabi Hamiltonian as a function of the coupling  $g$ . . . . . 36
- 4.2 The ground-state energy  $E_0$  of the resonant Rabi Hamiltonian as a function of the coupling  $g$  as determined via time-independent (Rayleigh-Schrödinger) perturbation theory. . . . 41
- 4.3 The expectation value  $\langle \sigma^z \rangle$  and the fluctuation  $\Delta \sigma^z$  in the even-parity  $\omega_0 = 0$  ground state  $|\Psi_+\rangle$  of the resonant Rabi Hamiltonian as a function of the coupling  $g$ . . . . . 43
- 4.4 The ground-state energy  $E_0$  of the resonant Rabi Hamiltonian as a function of the coupling  $g$  as determined via a variational calculation based on a mixed parity two-parameter coherent state, and via an even-parity projection after variation (PAV) based on the same state. . . . . 45
- 4.5 The expectation value  $\langle \sigma^z \rangle$  in the ground state of the resonant Rabi Hamiltonian, as determined via various variational calculations, as a function of the coupling  $g$ . . . . . 52

4.6	The expectation value $\langle b^\dagger b \rangle$ in the ground state of the resonant Rabi Hamiltonian, as determined via various variational calculations, as a function of the coupling $g$ . . . . .	53
4.7	The percentage error in the ground-state energy of the Rabi Hamiltonian obtained from the even-parity three-parameter PBV ansatz (4.41), as a function of the coupling $g/\omega$ and the two-level splitting $\omega_0/\omega$ . . . . .	58
4.8	The percentage error in the first excited state energy of the Rabi Hamiltonian obtained from the odd-parity three-parameter PBV ansatz (4.41), as a function of the coupling $g/\omega$ and the two-level splitting $\omega_0/\omega$ . . . . .	59
5.1	The ground-state energy $E_0$ of the resonant Rabi Hamiltonian as a function of the coupling $g$ as determined via an NCCM analysis based on Scheme I. . . . .	66
5.2	The critical coupling $g_c^{(N)}$ as a function of the level of approximation $N$ in the NCCM Scheme I analysis of the resonant Rabi Hamiltonian. . . . .	67
5.3	The ground-state energy $E_0$ of the resonant Rabi Hamiltonian as a function of the coupling $g$ as determined via an ECCM analysis based on Scheme I. . . . .	69
6.1	The expectation value of $\sigma_z$ in the ground state of the resonant Rabi Hamiltonian as a function of the coupling $g$ as determined via NCCM calculations based on Schemes I and III. . . . .	82

- 8.1 The percentage error in the ground-state energy of the scaled 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  $\omega_0$ . . . . . 119
- 8.2 Comparison of the ground-state expectation value  $\langle \sigma^z \rangle$  for the scaled 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, with the results of a CI diagonalization. . . . . 121
- 8.3 The percentage error in the first excited state energy of the scaled 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  $\omega_0$ . . . . . 125
- D.1 The behaviour of the three roots for the single CCM coefficient  $s_2^{(2)}$  in the even-parity SUB-2 NCCM Scheme I analysis of the scaled resonant Rabi Hamiltonian. . . . . 159

## List of Tables

4.1	Comparison of the results of a numerical diagonalization of the resonant Rabi Hamiltonian with a typical exact Juddian solution. . . . .	33
4.2	Comparison of the ground-state energy of the Rabi Hamiltonian obtained from an even-parity two-parameter PBV calculation with the results of a CI diagonalization in a basis of 101 even-parity states. . . . .	49
4.3	Comparison of the first excited state energy of the Rabi Hamiltonian obtained from an odd-parity two-parameter PBV calculation with the results of a CI diagonalization in a basis of 101 odd-parity states. . . . .	51
4.4	Comparison of the ground-state energy of the Rabi Hamiltonian obtained from an even-parity three-parameter PBV calculation with the results of a CI diagonalization in a basis of 101 even-parity states. . . . .	56
4.5	Comparison of the first excited state energy of the Rabi Hamiltonian obtained from an odd-parity three-parameter PBV calculation with the results of a CI diagonalization in a basis of 101 odd-parity states. . . . .	57



5.1	The behaviour of the SUB-3 ECCM Scheme I coefficients as a function of the coupling $g$ for the ground state of the resonant Rabi Hamiltonian. . . . .	71
6.1	The ground-state energy of the resonant Rabi Hamiltonian as a function of the coupling $g$ as determined via NCCM calculations based on Schemes III and IV. . . . .	80
6.2	The first excited state energy of the resonant Rabi Hamiltonian as a function of the coupling $g$ as determined via an NCCM calculation based on Scheme IV. . . . .	84
8.1	Comparison of the ground-state energy of the scaled linear $E \otimes e$ JT 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. . . . .	115
8.2	Comparison of the ground-state energy of the scaled 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, with the results of a CI diagonalization. . . . .	117
8.3	Comparison of the ground-state energy of the scaled 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, with the results of a CI diagonalization. . . . .	118

