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# Mercury Clusters

from van der Waals molecules to the metallic solid

A thesis submitted in partial fulfillment of the requirements of the degree  
of  
Doctor of Philosophy  
in  
Theoretical Chemistry  
at  
Massey University, Albany  
New Zealand.

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August 3, 2005

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# Abstract

The nature of mercury clusters is studied in an attempt to reconcile the behaviour of the solid with that of the smallest molecules. Related systems such as Zn, Cd, and Ba are investigated for comparison. A range of *ab initio* methods are employed, and their accuracy assessed. Density functional theory (DFT) based methods are shown to be unreliable. Different functionals vary widely in their description of a particular system, such as the dimer, while individual functionals vary in accuracy when applied across a range of system sizes. This is related to the neglect of van der Waals forces by DFT for the smaller systems, but raises interesting questions about the solid.

Wavefunction-based methods are seen to be much more reliable than DFT, although a high-level description of correlation is required. Hartree-Fock (HF) calculations are shown to be consistent in their description of systems of all sizes, and therefore although inadequate on its own the addition of a correlation potential derived from the many-body perturbational (MP2) calculation for the dimer corrects HF to produce exactly the correct bond lengths (when compared to the best known data) for all sizes up to the bulk lattice. The use of higher order many-body potentials is investigated and compared to the situation observed for the noble gases, since for small sizes these are the closest analogues of the neutral mercury clusters.

The question of how to simulate transitions in large clusters is addressed. Transitions of interest in clusters are the liquid to solid phase transition, the metal to non-metal transition, or a structural transition from one isomeric motif to another. Therefore the ability to calculate the properties of these clusters accurately is as important as the question of structure. Four-component DFT calculations for the mercury dimer polarisability agree well with the anisotropy derived from Raman spectroscopy.

Various isomers proposed in the literature are compared for the smaller mercury clusters. The structures of cationic clusters are also optimised, and their electronic excitation spectra are investigated through CIS(D) and TD-DFT calculations and

compared to experimental results. The structures of anionic zinc clusters are obtained and the density of states compared with experiment. The structures and spectra of these clusters are related to those seen for the magnesium analogues, and the effect of the  $d$ -electrons in perturbing the jellium model description of these clusters is considered.

# Acknowledgements

I wish to acknowledge the support of the Tertiary Education Commission in the form of a Top Achiever Doctoral scholarship. Thanks to the physics department at the Albert-Ludwigs-Universität, Freiburg, especially Dr Michael Moseler, Dr Bernd von Issendorf, and Professor Dr Hellmut Haberland. Thanks are also due to the Deutsche Akademische Austauschdienst.

I wish to thank Trond Saue for his hospitality in Strasbourg, and help with the frequency dependent polarisability calculations. I appreciate also the assistance of Beate Paulus with the work on solid mercury, for helpful discussions and material.

I am grateful to many coworkers who have helped at various stages of progress. In semi-chronological order, thanks go to Ralf Wesendrup, Gloria Moyano, Ivan Lim, Ralf Tonner, Johannes Gierlich, Tilo Söhnel, Radovan Bast, Bernd Huber, Robert Krawczyk, Behnam Assadollahzadeh, and Mattias Lein. Thanks to Inez Lees for ruthless editing advice.

By far the most important person to thank is my supervisor Peter Schwerdtfeger. Thank you for the privilege of working with you, and for the many useful discussions which I hope will be ongoing for some time yet.

# Contents

<b>1</b>	<b>Mercury, and clusters</b>	<b>1</b>
1.1	Mercury . . . . .	2
1.1.1	Relativistic effects . . . . .	3
1.1.2	Weak interactions and van der Waals bonds . . . . .	5
1.1.3	Simulations . . . . .	9
1.2	Clusters . . . . .	12
1.2.1	The jellium model . . . . .	13
1.2.2	The geometry of clusters . . . . .	15
1.2.3	Structural optimisation of clusters . . . . .	16
1.2.4	Experimental synthesis . . . . .	17
1.2.5	Spectra . . . . .	18
1.2.6	Charged clusters . . . . .	20
1.2.7	Metal cluster polarisabilities . . . . .	20
<b>2</b>	<b>Method review and the dimer potential</b>	<b>23</b>
2.1	Quantum mechanics and molecules . . . . .	24
2.2	Basis sets . . . . .	25
2.3	Hartree-Fock . . . . .	26
2.4	Density functional theory . . . . .	27
2.4.1	The Hohenberg-Kohn theorems . . . . .	28
2.4.2	The Kohn-Sham equations . . . . .	29
2.4.3	The local density approximation . . . . .	30
2.4.4	Spin in the local density approximation . . . . .	31
2.4.5	The exchange functional . . . . .	31
2.4.6	Density gradient corrections . . . . .	32
2.4.7	The Perdew-Wang 91 functional . . . . .	32
2.5	Møller-Plesset perturbation theory . . . . .	33

2.6	Coupled cluster theory . . . . .	35
2.6.1	CCSD(T) . . . . .	38
2.7	Pseudopotentials . . . . .	38
2.8	Dimers . . . . .	40
2.8.1	The Hg dimer . . . . .	40
2.8.2	The Cd dimer . . . . .	43
2.8.3	The Zn dimer . . . . .	45
2.8.4	The Ba dimer . . . . .	46
2.9	Basis set optimisation . . . . .	48
<b>3</b>	<b>Mercury dimer polarisability</b>	<b>51</b>
3.1	4-component calculations . . . . .	52
3.2	Molecular properties and linear response . . . . .	54
3.3	The calculation of the diatom polarisability . . . . .	58
3.3.1	Details . . . . .	58
3.3.2	Polarisabilities . . . . .	62
3.3.3	Second refractivity virial coefficient . . . . .	63
3.3.4	Comparison with experiment . . . . .	69
3.3.5	The simulation of the Raman spectrum . . . . .	71
3.4	Conclusions . . . . .	72
<b>4</b>	<b>Many-body decomposition</b>	<b>75</b>
4.1	Mercury . . . . .	77
4.2	Noble gases He, Ne, Ar, and Kr . . . . .	80
4.2.1	Helium . . . . .	80
4.2.2	Neon . . . . .	81
4.2.3	Argon . . . . .	84
4.2.4	Krypton . . . . .	87
4.3	Conclusions . . . . .	88
<b>5</b>	<b>Bulk mercury</b>	<b>91</b>
5.1	Density functional calculations . . . . .	92
5.1.1	Density of states . . . . .	98
5.1.2	Band structure . . . . .	98
5.1.3	Non-relativistic solid Hg . . . . .	104
5.2	Two-body forces and the bulk . . . . .	109
5.2.1	A two-body correlation potential . . . . .	109

5.3	Optimising the lattice with HF and correlation . . . . .	111
5.3.1	Scaling of the correlation potential . . . . .	112
5.4	Accuracy of the correlation potential . . . . .	114
5.5	Two-body correlation in small clusters . . . . .	116
5.6	Conclusions . . . . .	119
<b>6</b>	<b>Neutral Clusters</b>	<b>121</b>
6.1	Isomers . . . . .	121
6.1.1	Structural optimisation . . . . .	122
6.1.2	Lennard-Jones isomers . . . . .	122
6.1.3	Low symmetry isomers . . . . .	125
6.1.4	Hg <sub>7</sub> . . . . .	129
6.1.5	Tetrahedral isomers . . . . .	130
6.2	Energies . . . . .	131
6.3	Frequencies . . . . .	137
6.4	Optimised structures and the BSSE . . . . .	138
6.5	Polarisabilities . . . . .	139
<b>7</b>	<b>Cationic Clusters</b>	<b>145</b>
7.1	Isomers and relative stabilities . . . . .	147
7.2	Absorption spectra and CIS(D) calculations. . . . .	152
7.2.1	Basis set effects . . . . .	153
7.2.2	Excitation energies . . . . .	154
7.2.3	SAC-CI calculations . . . . .	161
7.2.4	SAC-CI for Hg <sub>3</sub> <sup>+</sup> and Hg <sub>4</sub> <sup>+</sup> . . . . .	162
7.2.5	A CIS comparison with other isomers . . . . .	165
7.3	Conclusions . . . . .	166
<b>8</b>	<b>Anionic Zinc Clusters</b>	<b>169</b>
8.1	Metal clusters and the jellium model . . . . .	169
8.2	Plane wave DFT and clusters . . . . .	170
8.3	Photoelectron spectra and the calculated density of states . . . . .	171
8.3.1	Isomers . . . . .	171
8.3.2	Comparison with experiment . . . . .	176
8.4	Conclusions . . . . .	180
<b>9</b>	<b>Conclusion</b>	<b>181</b>

<b>A</b>	<b>Basis sets</b>	<b>i</b>
A.1	Noble gases . . . . .	i
<b>B</b>	<b>Cartesian Coordinates</b>	<b>vii</b>
B.1	Lennard-Jones type Mercury clusters . . . . .	vii
B.2	Hartke isomers . . . . .	xix
B.3	Tetrahedral isomers . . . . .	xxvi
<b>C</b>	<b>Frequencies</b>	<b>xxvii</b>

# List of Figures

1.1	NR vs R CCSD(T) atomic polarisabilities . . . . .	6
1.2	NR vs R CCSD(T) atomic ionisation potentials . . . . .	7
1.3	The radial distribution function $g(r)$ . . . . .	11
1.4	The band gap . . . . .	12
1.5	Jellium model magic numbers . . . . .	19
2.1	Perfomance of various density functionals for the Hg dimer . . . . .	41
2.2	Perfomance of various methods for the Hg dimer. . . . .	42
2.3	Perfomance of DFT and other methods for the Cd dimer . . . . .	43
2.4	Perfomance of DFT and other methods for the Zn dimer . . . . .	46
2.5	Perfomance of DFT and other methods for the Ba dimer . . . . .	47
2.6	The dimer potential for Hg <sub>2</sub> with the small cc-basis. . . . .	49
3.1	A comparison of the dimer potentials. . . . .	58
3.2	Poles of the (LDA) frequency-dependent polarisability . . . . .	61
3.3	The static polarisability components . . . . .	64
3.4	The dynamic polarisability components . . . . .	65
3.5	The integrand in equation (3.50) with LDA $\alpha$ . . . . .	67
3.6	The integrand in equation (3.50) with B3LYP $\alpha$ . . . . .	67
3.7	Temperature dependence of $B(\omega, T)$ with LDA and B3LYP. . . . .	68
3.8	Temperature dependence of $\alpha(\omega, T)e^{-V(R)/kT}R^2$ , static LDA. . . . .	68
3.9	The static polarisability $\alpha$ and $\beta$ . . . . .	69
3.10	The frequency dependent polarisability $\alpha$ and $\beta$ . . . . .	70
3.11	Scaling of the static anisotropy . . . . .	71
3.12	Raman spectrum of Hg <sub>2</sub> . . . . .	72
3.13	Raman spectrum times the square of the Raman shift . . . . .	73
4.1	A X <sub>6</sub> octahedral cluster . . . . .	76

4.2	Distant dependent n-body contributions to $\text{Hg}_6$ . . . . .	78
4.3	The n-body contributions to $\text{Hg}_6$ . . . . .	79
4.4	Many-body decomposition for $\text{He}_6$ . . . . .	81
4.5	Many-body decomposition for $\text{Ne}_6$ . . . . .	82
4.6	$\text{Ne}_6$ DKH-CCSD(T) n-body component binding potentials . . . . .	83
4.7	$\text{Ne}_6$ DKH-CCSD(T) n-body contributions to $\text{Ne}_6$ . . . . .	84
4.8	Many-body decomposition for $\text{Ar}_6$ . . . . .	85
4.9	$\text{Ar}_6$ DKH-CCSD(T) many-body component binding energies. . . . .	86
4.10	$\text{Ar}_6$ DKH-CCSD(T) many-body components. . . . .	86
4.11	$\text{Ar}_6$ comparison of HF, MP2, MP3 and CCSD(T) . . . . .	87
4.12	$\text{Ar}_6$ comparison of MP2 and CCSD(T) . . . . .	88
4.13	Many-body decomposition for $\text{Kr}_6$ . . . . .	89
5.1	The rhombohedral primitive cell . . . . .	91
5.2	Solid mercury in the hexagonal cell . . . . .	92
5.3	The Hg lattice . . . . .	93
5.4	The PW91 potential curve for $\text{Hg}_2$ . . . . .	97
5.5	The DOS as obtained with HF and DFT. . . . .	99
5.6	Brillouin zone of mercury . . . . .	100
5.7	The Hartree-Fock band structure of mercury. . . . .	101
5.8	The B3LYP band structure of mercury. . . . .	101
5.9	The BP86 band structure of mercury. . . . .	102
5.10	The LDA band structure of mercury. . . . .	102
5.11	The PW91 band structure of mercury. . . . .	103
5.12	The PBE band structure of mercury. . . . .	103
5.13	The non-relativistic Hg dimer potential. . . . .	106
5.14	The non-relativistic LDA band structure of mercury. . . . .	107
5.15	The non-relativistic PW91 band structure of mercury. . . . .	108
5.16	The HF and correlation description of $\text{Hg}_2$ . . . . .	110
5.17	The HF and correlation energy vs $a$ . . . . .	112
5.18	The HF and correlation energy vs $c$ . . . . .	113
5.19	The HF and correlation energy vs scaling factor . . . . .	114
5.20	The HF potential and correlation potentials . . . . .	115
5.21	The HF potential for $N = 2 - 5$ . . . . .	116
5.22	The correlation potential for $N = 2 - 5$ . . . . .	117
5.23	The total (HF + correlation) potential for $N = 2 - 5$ . . . . .	118

6.1	Structures of ‘magic’ Lennard-Jones clusters . . . . .	123
6.2	Structures of small Hg Lennard-Jones type clusters . . . . .	124
6.3	LDA optimised structures of Hartke clusters . . . . .	125
6.4	MP2 optimised structures of the Hartke clusters . . . . .	126
6.5	The lowest energy structures of the two Hg <sub>7</sub> isomers. . . . .	129
6.6	Tetrahedral Hg <sub>10</sub> . . . . .	131
6.7	Total binding energy of LJ clusters. . . . .	132
6.8	Binding energy of LJ clusters per atom. . . . .	133
6.9	Binding energy of different isomers . . . . .	134
6.10	Energy difference between isomers . . . . .	135
6.11	Bond lengths of LJ clusters . . . . .	136
6.12	Energy and bond lengths . . . . .	136
6.13	Extrapolation to the bulk limit $E_{ZPVE}$ . . . . .	138
6.14	Polarisabilities and basis sets . . . . .	142
6.15	Polarisabilities of different isomers for $N = 7 - 14$ . . . . .	142
6.16	The PW91 polarisabilities of LJ clusters . . . . .	143
6.17	$\Delta\alpha$ as $\alpha(N) - \alpha(N - 1)$ . . . . .	144
6.18	$\Delta\alpha$ as $\alpha(N) - \alpha(N - 1)$ for different isomers . . . . .	144
7.1	Photoabsorption spectra of doubly charged mercury clusters . . . . .	145
7.2	Photoabsorption spectra of singly charged mercury clusters . . . . .	146
7.3	Photoabsorption energies . . . . .	147
7.4	Mercury cation structures . . . . .	148
7.5	The CIS and CIS(D) results compared to experiment. . . . .	160
7.6	Hg <sub>n</sub> <sup>+</sup> molecular orbitals . . . . .	161
7.7	CIS, CIS(D), and SAC-CI spectra for Hg <sub>n</sub> <sup>+</sup> . . . . .	164
7.8	Simulated spectra for Hg <sub>n</sub> <sup>+</sup> . . . . .	165
8.1	Properties of anionic Zn clusters . . . . .	172
8.2	Optimised isomers for Zn <sub>n</sub> <sup>-</sup> , $N = 5, \dots, 10, 12$ . . . . .	173
8.3	Ground state Zn <sub>n</sub> <sup>-</sup> clusters . . . . .	174
8.4	Density-of-states for Zn clusters, $N = 5 - 10, 12$ . . . . .	175
8.5	DOS and PES for $N = 7, 8, 9, 10, 12$ . . . . .	177
8.6	Core and valence orbitals for Zn <sub>10</sub> <sup>-</sup> . . . . .	179

# List of Tables

2.1	Large basis set used for $\text{Hg}_2$ . . . . .	40
2.2	Mercury relativistic pseudopotential . . . . .	41
2.3	Spectroscopic parameters for the Hg, Cd, Zn and Ba dimers . . . . .	44
2.4	Large basis set used for $\text{Cd}_2$ . . . . .	45
2.5	Large basis set used for $\text{Zn}_2$ . . . . .	45
2.6	Large basis set used for $\text{Ba}_2$ . . . . .	47
2.7	Small basis set used for $\text{Hg}_n$ . . . . .	48
2.8	Spectroscopic parameters of the Hg dimer . . . . .	50
3.1	DZ all-electron mercury basis set . . . . .	59
3.2	TZ all-electron mercury basis set . . . . .	60
3.3	The atomic polarisability . . . . .	62
3.4	The first three dimer Cauchy moments . . . . .	64
3.5	The second refractivity virial coefficients . . . . .	66
4.1	Many-body components of $\text{Hg}_6$ . . . . .	77
5.1	The basis set used for the DFT calculations . . . . .	95
5.2	Binding energies for bulk mercury obtained from DFT . . . . .	96
5.3	Lattice parameters for bulk mercury obtained from DFT . . . . .	96
5.4	The non-relativistic pseudopotential. . . . .	104
5.5	The non-relativistic basis set. . . . .	105
5.6	Non-relativistic lattice parameters . . . . .	107
5.7	Large uncontracted basis set for Hg. . . . .	110
5.8	Coefficients $a_{2n}$ of the correlation potential . . . . .	111
5.9	Lattice parameters obtained from HF + correlation . . . . .	111
5.10	The HF + correlation optimised clusters $N = 2 - 6$ . . . . .	118

6.1	Optimised LJ isomers . . . . .	127
6.2	Optimised Hartke isomers. . . . .	128
6.3	Optimised parameters for the Hg <sub>7</sub> isomers. . . . .	130
6.4	A comparison of the PW91 structures for Hg <sub>10</sub> . . . . .	131
6.5	BSSE and spin-orbit interaction, estimated for $N = 2 - 6$ . . . . .	139
6.6	A summary of optimised Hg <sub><math>N</math></sub> for $N = 2 - 6$ . . . . .	140
6.7	The PW91 atomic polarisability . . . . .	140
6.8	The polarisability basis set for Hg (small+spf). . . . .	141
7.1	LDA optimised Hg cations. . . . .	150
7.2	PW91 optimised Hg cations. . . . .	150
7.3	MP2 optimised Hg cations. . . . .	151
7.4	Binding energies for the different Hg <sub><math>N</math></sub> <sup>+</sup> isomers . . . . .	151
7.5	Basis set comparison for Hg <sub>3</sub> <sup>+</sup> . . . . .	153
7.6	The excitation energies and oscillator strengths of Hg <sub>3</sub> <sup>+</sup> . . . . .	154
7.7	The excitation energies and oscillator strengths of Hg <sub>4</sub> <sup>+</sup> . . . . .	155
7.8	The excitation energies and oscillator strengths of Hg <sub>5</sub> <sup>+</sup> . . . . .	156
7.9	The excitation energies and oscillator strengths of Hg <sub>6</sub> <sup>+</sup> . . . . .	157
7.10	The excitation energies and oscillator strengths of Hg <sub>7</sub> <sup>+</sup> . . . . .	158
7.11	The excitation energies and oscillator strengths of Hg <sub>8</sub> <sup>+</sup> . . . . .	159
7.12	SAC-CI energies and oscillator strengths of Hg <sub>3</sub> <sup>+</sup> . . . . .	163
7.13	SAC-CI energies and oscillator strengths of Hg <sub>4</sub> <sup>+</sup> . . . . .	163
7.14	A comparison of isomers for Hg <sub>5</sub> <sup>+</sup> . . . . .	167
7.15	A comparison of isomers for Hg <sub>6</sub> <sup>+</sup> . . . . .	168
A.1	Basis set used for helium . . . . .	ii
A.2	Basis set used for neon . . . . .	iii
A.3	Basis set used for argon . . . . .	iv
A.4	Basis set used for krypton - $s$ -functions . . . . .	v
A.5	Basis set used for krypton - $p, d, f, g$ -functions . . . . .	vi
B.1	Coordinates for LDA optimised LJ isomers. ( $N = 1 - 6$ ) . . . . .	viii
B.2	Coordinates for LDA optimised LJ isomers. ( $N = 7 - 10$ ) . . . . .	ix
B.3	Coordinates for LDA optimised LJ isomers. ( $N = 11 - 12$ ) . . . . .	x
B.4	Coordinates for LDA optimised LJ isomers. ( $N = 11 - 12$ ) . . . . .	xi
B.5	Coordinates for MP2 optimised LJ isomers. ( $N = 2 - 6$ ) . . . . .	xii
B.6	Coordinates for MP2 optimised LJ isomers. ( $N = 7 - 9$ ) . . . . .	xiii

B.7	Coordinates for CCSD(T) optimised LJ isomers . . . . .	xiv
B.8	Coordinates for small PW91 clusters . . . . .	xv
B.9	Coordinates for PW91 clusters $N = 7 - 10$ . . . . .	xvi
B.10	Coordinates for PW91 clusters $N = 11 - 12$ . . . . .	xvii
B.11	Coordinates for PW91 clusters $N = 13 - 14$ . . . . .	xviii
B.12	Coordinates for LDA Hartke isomers. ( $N = 7 - 10$ ) . . . . .	xix
B.13	Coordinates for LDA Hartke isomers. ( $N = 11-12$ ) . . . . .	xx
B.14	Coordinates for LDA Hartke isomers. ( $N = 13-14$ ) . . . . .	xxi
B.15	Coordinates for MP2 Hartke isomers . . . . .	xxii
B.16	Coordinates for CCSD(T) Hartke isomers . . . . .	xxii
B.17	Coordinates for PW91 Hartke isomers $N = 7 - 10$ . . . . .	xxiii
B.18	Coordinates for PW91 Hartke isomers $N = 11 - 12$ . . . . .	xxiv
B.19	Coordinates for PW91 Hartke isomers $N = 13 - 14$ . . . . .	xxv
B.20	Coordinates for PW91 Tetrahedral $Hg_{10}$ . . . . .	xxvi
C.1	Frequencies for $N = 1 - 6$ . . . . .	xxvii
C.2	LJ Frequencies for $N = 7,8$ . . . . .	xxviii
C.3	LJ Frequencies for $N = 9$ . . . . .	xxix
C.4	LJ Frequencies for $N = 10$ . . . . .	xxx
C.5	LJ Frequencies for $N = 11$ . . . . .	xxxi
C.6	LJ Frequencies for $N = 12$ . . . . .	xxxii
C.7	LJ Frequencies for $N = 13$ . . . . .	xxxiii
C.8	LJ Frequencies for $N = 14$ . . . . .	xxxiv
C.9	Hartke Frequencies for $N = 7,8$ . . . . .	xxxv
C.10	Hartke Frequencies for $N = 9$ . . . . .	xxxvi
C.11	Hartke Frequencies for $N = 10$ . . . . .	xxxvii
C.12	Hartke Frequencies for $N = 11$ . . . . .	xxxviii
C.13	Hartke Frequencies for $N = 12$ . . . . .	xxxix
C.14	Hartke Frequencies for $N = 13$ . . . . .	xl
C.15	Hartke Frequencies for $N = 14$ . . . . .	xli
C.16	Frequencies for tetrahedral $N = 10$ . . . . .	xlii