

*Ab Initio* Investigation of the Electronic  
Structure and Rovibrational Spectroscopy of  
Group-I and II Metal Hydrides and Helides

A Thesis Presented for the Degree of Doctor of Philosophy

at

The University of Newcastle

by

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## Declaration

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(Signed) \_\_\_\_\_

Alister James Page

2008

To Mardi and my family.

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## Abstract

The electronic structure and rovibrational spectroscopy of  $\text{MH}_2$ ,  $\text{MH}_2^{n+}$ ,  $\text{HMHe}^{n+}$  and  $\text{MHe}_2^{n+}$  ( $\text{M} = \text{Li, Be, Na, Mg, K, Ca}$ ;  $n = 1, 2$ ) have been investigated using correlated *ab initio* ansatz.

In order to determine the efficacy of various electronic structure methods with respect to Group-I and II hydrides and helides, atomic properties of Li, Be, Na, Mg, K and Ca were calculated. Relativistically-corrected UCCSD(T) and IC-MRCI(+Q) were deemed to be the most suitable ansatz with respect to both efficiency and accuracy. The lowest  ${}^2\text{A}_1$  and  ${}^2\Sigma^-$  states of  $\text{MH}_2$  were found to be purely repulsive, in agreement with previous predictions. The main factor determining the structure and stability of the excited states of  $\text{MH}_2$  was the relative orientations and occupations of the valence  $p$  atomic orbital of M and the  $\text{H}_2$   $1\sigma_u$  orbital. The ground states of  $\text{MH}_2^{n+}$  were found to be the result of the charge-quadrupole interaction between  $\text{M}^{n+}$  and the  $\text{H}_2$  molecular subunit. The structures of the ground states of  $\text{HMHe}^+$  were extremely fluxional with respect to the central bond angle co-ordinate. The ground state PESs of  $\text{MHe}_2^+$  were also extremely sensitive to the *ab initio* ansatz by which they are modelled. The respective bonding of the H and He in both  $\text{HMHe}^+$  and  $\text{HMHe}^{2+}$  appeared to be charge-dependent in the case of Be, Mg and Ca. Despite the weak bonding observed for the Group-II hydrohelide and helide monocations, the corresponding dications each exhibit thermodynamically stable equilibria.

The solution algorithm of von Nagy-Felsobuki and co-workers was employed in the calculation of vibrational and rovibrational spectra. This algorithm employed an Eckart-Watson Hamiltonian in conjunction with rectilinear normal co-ordinates.

Vibrational and rovibrational Hamiltonian matrices were diagonalised using variational methods. This algorithm was extended so that the vibration transition moment integrals, and hence vibrational radiative properties, of linear triatomic molecules could be calculated. A method by which vibration-averaged structures are calculated was also developed and implemented.

Analytical potential energy functions (PEFs) and dipole moment functions (DMFs) of  $(^1A_1)\text{LiH}_2^+$ ,  $(^1A_1)\text{NaH}_2^+$ ,  $(^1A_1)\text{BeH}_2^{2+}$ ,  $(^1A_1)\text{MgH}_2^{2+}$ ,  $(^1\Sigma_g^+)\text{BeHe}_2^{2+}$ ,  $(^2\Sigma^+)\text{HBeHe}_2^{2+}$ ,  $(^1\Sigma_g^+)\text{MgHe}_2^{2+}$  and  $(^2\Sigma^+)\text{HMgHe}_2^{2+}$  were developed using least-square regression techniques in conjunction with discrete *ab initio* grids. Vibrational structures and spectra of these species were subsequently calculated. In addition, the rovibrational spectra of  $(^1A_1)\text{LiH}_2^+$ ,  $(^1A_1)\text{NaH}_2^+$ ,  $(^1A_1)\text{BeH}_2^{2+}$  and  $(^1A_1)\text{MgH}_2^{2+}$  were calculated. For  $(^1A_1)\text{LiH}_2^+$  and  $(^1A_1)\text{LiD}_2^+$ , calculated rovibrational transition frequencies for  $J \leq 10$  and  $0 \leq K \leq 3$  were within *ca.* 0.1-0.2% of experimental values.

## Publications Related to this Thesis

- [1] *Ab initio properties and potential energy surface of the ground electronic state of BeHe<sub>2</sub><sup>+</sup>*. A. J. Page, D. J. D. Wilson, E. I. von Nagy-Felsobuki, *Chem. Phys. Lett.*, (2006) **429**(1-3) 335.
- [2] *Rovibrational spectra of LiH<sub>2</sub><sup>+</sup>, LiHD<sup>+</sup> and LiD<sub>2</sub><sup>+</sup> determined from FCI property surfaces*. A. J. Page, E. I. von Nagy-Felsobuki, *J. Phys. Chem. A*, (2007) **111**(20) 4478.
- [3] *Ab initio calculations of the ground electronic states of HBeHe<sup>+</sup> and BeHe<sub>2</sub><sup>2+</sup>*. A. J. Page, D. J. D. Wilson, E. I. von Nagy-Felsobuki, *Chem. Phys. Lett.*, (2007) **442**(4-6) 194.
- [4] *Ab initio rovibrational spectra of BeH<sub>2</sub><sup>2+</sup>, BeHD<sup>2+</sup> and BeD<sub>2</sub><sup>2+</sup>*. A. J. Page, E. I. von Nagy-Felsobuki, *Mol. Phys.*, (2007) **105**(19-22) 2527.
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- [11] *Group-I and II hydride cations: an ab initio investigation*. A. J. Page, D. J. D. Wilson, E. I. von Nagy-Felsobuki, *J. Phys. Chem. A*, (Submitted).

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- [1] *Ab initio rovibrational spectra of singly charged lithium hydrides using full configuration interaction property surfaces.* A. J. Page, E. I. von Nagy-Felsobuki, *6th Royal Australian Chemical Institute Conference on Physical Chemistry (CPC2007)*, Abstract Page PC11 P19, Adelaide, Australia (2007).
- [2] *Ab initio properties and potential energy surface of the ground electronic state of BeHe<sub>2</sub><sup>+</sup>.* A. J. Page, D. J. D. Wilson, E. I. von Nagy-Felsobuki, *6th Royal Australian Chemical Institute Conference on Physical Chemistry (CPC2007)*, Abstract Page PP26 P44, Adelaide, Australia (2007).
- [3] *Ab initio rovibrational spectrum of BeH<sub>2</sub><sup>2+</sup> using IC-MRCI property surfaces.* A. J. Page, E. I. von Nagy-Felsobuki, *Molecular Quantum Mechanics: Analytical Gradients and Beyond. A Conference in Honour of Peter Pulay*, Abstract Page 35, Budapest, Hungary (2007).
- [4] *An ab initio study of ground state MH<sub>2</sub>, HMHe<sup>+</sup> and MHe<sub>2</sub><sup>2+</sup>, M = Mg, Ca.* A. J. Page, E. I. von Nagy-Felsobuki, *Singapore International Chemistry Conference 5 (SICC-5)*, Abstract Page 2:32, Singapore (2007).
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- [7] *Molecular ion-quadrupole complexes: Group I/II ion dihydride cations*. A. J. Page, D. J. D. Wilson, E. I. von Nagy-Felsobuki, *22<sup>nd</sup> Austin Symposium on Molecular Structure*, Abstract Page P25, Austin, Texas, USA (2008).
- [8] *Ab initio rovibrational spectra of ion-quadrupole complexes*. A. J. Page, E. I. von Nagy-Felsobuki, *2008 World Congress of WATOC*, Abstract Page P0027, Sydney, Australia (2008).
- [9] *Ab initio trends in the structures and stabilities of  $MH_2^{n+}$  ( $M = Li-K, Be-Ca$ ;  $n = 1, 2$ )*. A. J. Page, D. J. D. Wilson, E. I. von Nagy-Felsobuki, *2008 World Congress of WATOC*, Abstract Page OC041, Sydney, Australia (2008).

## Table of Acronyms

<b>ANO</b>	Atomic NO
<b>ANO-RCC</b>	Relativistically corrected ANO basis set
<b>AO</b>	Atomic orbital
<b>aug-cc-pCVXZ</b>	Augmented cc-pCVXZ basis set
<b>aug-cc-pVXZ</b>	Augmented cc-pVXZ basis set
<b>aug-CVQZ</b>	Augmented CVQZ basis set
<b>BO</b>	Born-Oppenheimer
<b>BP</b>	Breit-Pauli
<b>BSSE</b>	Basis set superposition error
<b>CASSCF</b>	Complete active space SCF
<b>CBS</b>	Complete basis set
<b>cc</b>	Correlation consistent
<b>cc-pCVXZ</b>	cc with polarisation, core and valence X- $\zeta$ basis set
<b>cc-pVXZ</b>	cc with polarisation, valence X- $\zeta$ basis set
<b>CC</b>	Coupled-cluster
<b>CCSD</b>	CC with single and double excitations
<b>CCSD(T)</b>	CCSD with perturbative treatment of triple excitations
<b>CCSDT</b>	CCSD with ‘full’ triple excitations
<b>CCSDTQ</b>	CCSDT with quadruple excitations
<b>CG</b>	Cowan-Griffin
<b>CGTO</b>	Contracted GTO
<b>CI</b>	Configuration interaction
<b>CIS</b>	CI with single excitations

<b>CISD</b>	CI with single and double excitations
<b>CISDT</b>	CISD with ‘full’ triple excitations
<b>CISDTQ</b>	CISDT with quadruple excitations
<b>CVXZ</b>	Core-valence polarisation X- $\zeta$ basis set
<b>Darw</b>	Relativistic Darwin correction
<b>DFT</b>	Density functional theory
<b>DHF</b>	Dirac-Hartree-Fock
<b>DK</b>	Douglas-Kroll
<b>DK<math>n</math></b>	$n^{\text{th}}$ order DK correction
<b>DMS</b>	Dipole moment surface
<b>DMF</b>	Dipole moment function
<b>DUN</b>	Dunham
<b>DZ</b>	Double- $\zeta$
<b>ECP</b>	Effective core potential
<b>EDUN</b>	Exponential Dunham
<b>ESR</b>	Electron spin resonance
<b>EOGL</b>	Exponential Ogilvie
<b>ESPF</b>	Exponential Simons, Parr and Finlan
<b>FCI</b>	Full CI
<b>FEM</b>	Finite element method
<b>FTIR</b>	Fourier Transform IR
<b>GTO</b>	Gaussian type orbital
<b>HEG</b>	Harris, Engerholm and Gwinn
<b>HF</b>	Hartree-Fock

<b>HOMO</b>	Highest occupied MO
<b>IC-MRCI</b>	Internally contracted MRCI
<b>IE</b>	Ionisation energy
<b>IE<sub><i>n</i></sub></b>	<i>n</i> <sup>th</sup> IE
<b>IR</b>	Infra-red
<b>LUMO</b>	Lowest unoccupied MO
<b>MED</b>	Maximum electron density
<b>MEP</b>	Minimum energy path
<b>MCSCF</b>	Multi-configurational SCF
<b>MO</b>	Molecular orbital
<b>MP</b>	Møller-Plesset
<b>MP<sub><i>n</i></sub></b>	<i>n</i> <sup>th</sup> order Møller-Plesset
<b>MP4(SDTQ)</b>	‘Full’ MP4 with single, double, triple, quadruple excitations
<b>MRCI</b>	Multi-reference CI
<b>MRCISD</b>	MRCI with single and double excitations
<b>MV</b>	Relativistic mass-velocity correction
<b>NO</b>	Natural orbital
<b>OGL</b>	Ogilvie
<b>PES</b>	Potential energy surface
<b>PEF</b>	Potential energy function
<b>+Q</b>	Davidson correction ( <i>viz.</i> CISD+Q/MRCISD+Q)
<b>QCI</b>	Quadratic CI
<b>QCISD</b>	QCI with single and double excitations
<b>QCISD(T)</b>	QCISD with perturbative treatment of triple excitations

<b>QZ</b>	Quadruple- $\zeta$
<b>RG</b>	Rare gas
<b>RHF</b>	Spin-restricted HF
<b>ROHF</b>	Spin-restricted open-shell HF
<b>SCF</b>	Self consistent field
<b>SD</b>	Slater determinant
<b>SO</b>	Spin-orbit
<b>SPF</b>	Simons, Parr and Finlan
<b>SSFC</b>	Site-site function counterpoise
<b>STO</b>	Slater type orbital
<b>SVD</b>	Singular value decomposition
<b>TM</b>	Transition metal
<b>TZ</b>	Triple- $\zeta$
<b>UCCSD</b>	Spin-unrestricted CCSD
<b>UCCSD(T)</b>	Spin-unrestricted CCSD(T)
<b>UCCSDT</b>	Spin-unrestricted CCSDT
<b>UHF</b>	Spin-unrestricted HF
<b>UV</b>	Ultra-violet
<b>VB</b>	Valence bond
<b>VBO</b>	Vibration band origin
<b>ZPE</b>	Zero-point energy