Chapter One

Introduction

Rigorous comparison of theoretical results with experiment is of paramount importance to *ab initio* quantum chemistry. Not only does the process facilitate calibration of theoretical procedures, it also permits insight into the information able to be extracted from particular experiments, leads to an understanding of experimental limitations and an appreciation of difficulties faced by experimenters in the measurement process. The ultimate aim of *ab initio* theory [1, 2] is to possess the ability to model experimental conditions, without recourse to any data other than the fundamental constants. To achieve this objective, it is necessary to strongly delineate the differences between theory and experiment. Practical ways of modelling physical phenomena can then be developed by encompassing, within a theoretical prediction, all effects that contribute to an experimental observation.

The range of molecular properties open to routine calculation by the *ab initio* quantum chemist is enormous: molecular geometries, vibrational frequencies, dipole and quadrupole moments, magnetizabilities, nuclear spin-spin coupling constants and NMR shielding constants are but a few of them [3]. The primary focus of the present thesis involves the exploration of the effects of vibrational and rotational motion on electrical molecular properties such as dipole and quadrupole moments, polarizabilities and polarizability anisotropies. The choice of molecular properties for study has been strongly guided by interest and previous experience in the *ab initio* calculation of electrical properties [4-9]. However, it should be stressed that in many instances, the theoretical framework is entirely general and may be broadened, in a straightforward manner, to include other molecular properties such as octopole moments, magnetizabilities, electric-field gradients at nuclei, and first and second electrical hyperpolarizabilities. Consequently, a concerted

attempt is made to utilise the concept of a general molecular property in theoretical equations.

Theoretical calculations of electrical properties are most often carried out at a fixed nuclear configuration with clamped nuclei. Vibrational and rotational motion are completely neglected such that a calculated molecular property corresponds to the observable for an isolated molecule in the gas-phase, with clamped nuclei, at 0 K. It is therefore questionable as to whether a comparison of such theoretical results with experimental estimates is valid, if the effects of rotational and vibrational motion are neglected from the theoretical prediction.

A vast number of techniques have been developed for measuring electrical properties and several fine reviews have been published. Methods used for extracting molecular moments and polarizabilities from experimental data have been reviewed by Buckingham [10-12], Bogaard and Orr [13], Gray and Gubbins [14] and Shelton and Rice [15]. Compilations of experimental electric dipole moments include those of McClellan [16] and Gordy and Cook [17]. Molecular beam studies for determination of electric dipole and quadrupole moments have been outlined by Dymanus [18] and Dyke and Muenter [19].

To appreciate the role of theory in the successful comparison with experiment, it is necessary to briefly describe the experiments for determining electrical properties and the experimental conditions for such measurements. Experiments designed for gas-phase measurement of electrical properties normally involve the presence of electric fields and field-gradients or magnetic fields [11, 12, 20-24]. An optical laser of known wavelength is often an integral part of the experimental apparatus, either for detecting optical birefringence or as a source of an oscillating electric field. The majority of gas-phase experiments are carried out at temperatures within the range 100-500 K, although some refractivity measurements have been performed at temperatures close to 1000 K [25-28]. Rayleigh light scattering measurements [22, 29-31], the optical Kerr effect [24, 32-35], electric field-gradient induced birefringence experiment [21, 36-39], and the gas-phase Cotton-Mouton effect [40-42] all fall into this broad category of experiments. Refractivity and Rayleigh light scattering experiments [13] yield dynamic polarizabilities and polarizability anisotropies corresponding to optical wavelengths in the range 400-700 nm. Dipole moment and quadrupole moment determinations from molecular beam methods [19] are rotational-vibrational state dependent and require the influence of electric fields or field-gradients. Recent advances in technology have led to molecular beam electric resonance (MBER) and laser microwave double resonance (LMDR) measurements of electrical dipole moments of

molecules for several excited rotational-vibrational states [43, 44]. Molecular Zeeman effect quadrupole moment measurements [45-49] for non-dipolar molecules are usually performed on an isotopically substituted species, such as CH_2CD_2 for ethene [50]. The effect of an electric field on the nuclear motion may also need to be considered for some properties. Second-order Stark effect [12, 51-56], dielectric constant [57-59] and Kerr effect measurements [35, 60, 61] allow determination of dipole polarizabilities that include vibrational contributions from the influence of the external electric field.

Considering the range of different experiments, a theoretical approach to mimic experimental conditions for electrical and magnetic properties should ideally include the capability for calculation of:

- accurate vibrationless properties at an appropriate reference geometry;
- a correction for the effect of zero-point vibrational motion on a property;
- properties in excited vibrational-rotational states;
- properties of isotopically substituted molecules;
- properties at a given temperature;
- frequency dependence of certain dynamic properties, e.g. polarizability; and
- a correction for the effect of an electric field on nuclear motion.

One or more of these quantities may need to be included in a theoretical prediction to adequately model electrical properties derived from certain experiments. The selection of appropriate contributions is obviously dictated by the experimental conditions. Inherent accuracy and precision of particular experiments must also be carefully assessed, especially for experimental quantities possessing large uncertainties. In many cases, it may be sufficient to compute a correction for the effects of zero-point vibrational motion on a property to obtain quantitative agreement with experiment (within experimental uncertainties), thereby making redundant the inclusion of further temperature or rotational corrections. Zero-point vibrational corrections are expected to be more important than thermal and rotational corrections. The latter two are likely to be necessary for extremely accurate theoretical predictions or situations where the agreement between accurate theory and experiments is particularly poor and an explanation for the discrepancies is sought. It should be noted that the magnitude and sign of vibrational, rotational and thermal contributions to electrical properties is usually difficult to predict in an *a priori* sense. Therefore, *ab initio* methods play an important role in obtaining reliable estimates of the vibrational and rotational contributions. Theoretical requirements, listed above for an

approach to obtain quantitative agreement with experiment, are now examined in greater detail.

A starting point for obtaining accurate theoretical predictions, to be quantitatively compared with experimental quantities, involves calculation of accurate vibrationless properties at a suitable reference geometry. The process is relatively straightforward with good quality *ab initio* codes [62-64] equipped with sophisticated electron-correlation treatments, especially if an accurate reference geometry is available, either from experiment or from high-level *ab initio* theory. Exceptionally accurate studies may require considerable computational resources but it is undoubtedly clear that unless the "uncorrected" properties are reliable, the application of vibrational and rotational corrections is likely to be of limited use.

One of the most important effects to be included in a theoretical prediction is a correction, to an observable property, for the effects of vibrational motion. Purely a quantum mechanical effect, zero-point vibrational motion is a result of particle confinement (induced by a potential) and its existence can be explained by the Heisenberg uncertainty principal [65]. Zero-point vibrational effects manifest themselves in thermodynamics [66], crystal structure [67], molecular structure [68, 69], intermolecular forces [70] and spectroscopy [71, 72]. The process required for modelling the effects of vibrational motion on a property involves averaging the electronic property over vibrational wavefunctions (vibrational averaging). Zero-point vibrational averaging (ZPVA) studies and associated zero-point vibrational corrections (ZPVCs), defined as the difference between the rotationless vibrational ground-state electrical property and the equilibrium property, have been used to provide theoretical predictions that are more closely compatible with experimental results. Vibrational averaging studies of electrical properties have been carried out for polyatomic molecules CH_4 [73-77], NH_3 [78, 79], H_2O [80-83], CO_2 [84], C_2H_2 [85] and C_2H_4 [76]. A vast number of calculations have been carried out for diatomic molecules, since they represent the simplest possible case [53, 76, 86-92]. Vibrational averaging studies on larger molecules are scarce and this is predominantly due to the high computational effort required.

Properties in excited rotational-vibrational states are closely allied to the vibrational ground state corrections. Theoretical requirements for these calculations are expected to be similar to those for ZPVCs, but improved accuracy in both energy and property surfaces is necessary for the properties of molecules in highly-excited rotational-vibrational states. Effects of isotopic substitution [74, 93-95] and temperature [95] on electrical properties have

not been adequately investigated via theoretical methods. Certainly, isotope effects on the properties of large molecules represent an almost entirely unexplored branch of theoretical chemistry.

Dynamic polarizabilities have been well explored and the theoretical *ab initio* methods for such calculations are firmly established [96-101]. Relatively fewer *ab initio* calculations of the effect of an electric field on nuclear motion have been presented for polyatomic molecules [84, 102]. Recently, perturbation formulae for the pure vibrational contributions to electrical response properties have been published [84, 103-105] and this may lead to further studies of these potentially important effects. Although the influence of an electric field on nuclear motion may only be relevant to certain experiments for low-order response properties such as the dipole-polarizability, the pure vibrational higher-order hyperpolarizabilities are especially significant [102, 103] in the comparison of theory with experiment.

Within the Born-Oppenheimer approximation [106], all of the properties able to be calculated by *ab initio* means are dependent upon the nuclear configuration or the molecular geometry. Through separation of electronic, vibrational and rotational motions, the nuclear positions enter the electronic Schrödinger equation as parameters, not variables. In doing so, the concept of a property surface is unavoidably encountered, since calculation of a given property as a function of nuclear displacements leads to a multidimensional surface or property (hyper)surface [3, 82, 107, 108]. The property surfaces for the molecule then provide a vast amount of information about the chemical and physical behaviour of the molecule.

Specifically, derivatives of the property surfaces with respect to nuclear displacements are necessary for calculation of many of the contributions outlined above. It is likely that the lack of a "black-box" approach for calculation of property derivatives is the primary reason for the small number of studies concerning the effects of vibrational and rotational motion on molecular properties. A number of *ab initio* programs possess the ability to calculate energy second derivatives and electrical property first-derivatives (such as dipole moment and polarizability first-derivatives) [62] but it is quite rare or even impossible to find *ab initio* quantum chemistry codes incorporating the calculation of third- and fourth-order energy and property derivatives.

With these considerations in mind, the main focus of the present thesis involves the development of a routine theoretical approach for calculation of vibrational and rotational contributions to electrical properties. Theory for properties in rotational-vibrational states,

pure vibrational polarizabilities and isotope effects on molecular properties is presented in Chapter 2 along with the background required for vibrational-rotational spectroscopy. Methods for calculation of energy and property derivatives are investigated in Chapter 3 with a detailed description of a least-squares approach and a central-differences scheme for computing general property derivatives. Other useful and relevant theoretical procedures for electrical property studies, such as an approximate method for obtaining frequency dependent polarizabilities that takes into account the effects of electron correlation, are described in Chapter 3. Basis sets for electrical properties are also discussed in Chapter 3 and a novel method based upon MP2 atomic natural orbitals is used in the construction of a number of basis sets. Theoretical and computational methods are then applied to a set of molecules comprising the second-row hydrides (SiH_4, PH_3, H_2S, HCl), fluoromethanes (CF_4, CHF_3, CH_2F_2, CH_3F), acetylene (C_2H_2), ethene (C_2H_4) and ethane (C_2H_6). These molecules have been chosen because of their relatively small size and the availability of experimental data.

Ab initio determination of accurate electrical properties and assessment of the requirements for such predictions is a strong theme of the thesis: basis set and level of theory requirements, the necessity of ZPVCs, pure vibrational polarizabilities, rotational corrections, thermal effects and the effect of isotopic substitution on electrical properties are all established from studies presented within. The ZPVCs to the electrical properties receive the most attention as they play a fundamental role in achieving quantitative agreement of theory with experiment. It is intended that the application of the theory to the above molecular systems will assist in establishing the sign and magnitude of ZPVCs, the accuracy of computed pure vibrational polarizabilities and help illustrate the general application of the methods described in the present thesis. It is also necessary to establish at what stages of the theoretical predictive process certain approximations can be utilised and determine the loss in accuracy incurred from their use. Once the approximations have been well tested for smaller polyatomic molecules, they may then be applied to larger systems with confidence.

A particularly heavy emphasis is placed on comparison of theoretical results with experiment. Whenever possible, experimental observables are directly computed from theoretical predictions to avoid mixing information from different experiments. For example, the Rayleigh depolarization ratio, ρ_0, is usually converted to a polarizability anisotropy using an experimentally derived mean polarizability [13, 29, 109]. The approach often taken in the present thesis involves direct theoretical calculation of the observable, in this case, ρ_0; this procedure is expected to be less error prone than the process of comparing

indirect experimental measurements with theory. It is hoped that through performing detailed comparisons between theory and experiment, a stronger collaboration between theoreticians and experimentalists can be attained to help resolve some of the discrepancies uncovered in the present thesis.

References

[1] Hehre, W. J., Radom, L., Schleyer, P. v. R., and Pople, J. A., 1986, *Ab Initio Molecular Orbital Theory* (John Wiley & Sons).

[2] Head-Gordon, M., 1996, *J. phys Chem.*, **100**, 13213.

[3] Fowler, P. W., 1987, *Annu. Rep. Prog. Chem. Sect. C.*, **84**, 3.

[4] Spackman, M. A., 1989, *J. phys Chem.*, **93**, 7594.

[5] Spackman, M. A., 1989, *Chem. Phys. Lett.*, **161**, 285.

[6] Spackman, M. A., 1991, *J. chem. Phys.*, **94**, 1288.

[7] Spackman, M. A., 1991, *J. chem. Phys.*, **94**, 1295.

[8] Coonan, M. H., Craven, I. E., Hesling, M. R., Ritchie, G. L. D., and Spackman, M. A., 1992, *J. phys Chem.*, **96**, 7301.

[9] Dougherty, J., and Spackman, M. A., 1994, *Molec. Phys.*, **82**, 193.

[10] Buckingham, A. D., 1967, *Adv. chem. Phys.*, **12**, 107.

[11] Buckingham, A. D., 1972, In *MTP International Review of Science, Physical Chemistry Series 1*, Vol. 2, edited by A. D. Buckingham and G. Allen (Butterworths), p. 241.

[12] Buckingham, A. D., 1972, In *MTP International Review of Science, Physical Chemistry Series 1*, Vol. 3, edited by D. A. Ramsay (Butterworths), p. 73.

[13] Bogaard, M. P., and Orr, B. J., 1975, In *International Review of Science, Physical Chemistry Series 2*, Vol. 2, edited by A. D. Buckingham (Butterworths), p. 149.

[14] Gray, C. G., and Gubbins, K. E., 1984, *Theory of Molecular Fluids. Volume 1: Fundamentals* (Clarendon Press).

[15] Shelton, D. P., and Rice, J. E., 1994, *Chem. Rev.*, **94**, 3.

[16] McClellan, A. L., 1989, *Tables of Experimental Dipole Moments* (Rahara Enterprises).

[17] Gordy, W. L., and Cook, R. L., 1984, *Microwave Molecular Spectra* (Wiley).

[18] Dymanus, A., 1975, In *International Review of Science, Physical Chemistry Series 2*, Vol. 3, edited by A. D. Buckingham (Butterworths), p. 127.

[19] Dyke, T. R., and Muenter, J. S., 1975, In *International Review Of Science, Physical Chemistry Series 2*, Vol. 2, edited by A. D. Buckingham (Butterworths), p. 27.

[20] Buckingham, A. D., and Pople, J. A., 1956, *Proc. Phys. Soc. B*, **69**, 1133.

[21] Buckingham, A. D., 1959, *J. chem. Phys.*, **30**, 1580.

[22] Bridge, N. J., and Buckingham, A. D., 1966, *Proc. R. Soc. Lond. A*, **295**, 334.

[23] Buckingham, A. D., 1959, *Quart. Rev.*, **13**, 183.

[24] Buckingham, A. D., Bogaard, M. P., Dunmur, D. A., Hobbs, C. P., and Orr, B. J., 1970, *Trans. Faraday Soc.*, **66**, 1548.

[25] Hohm, U., and Kerl, K., 1990, *Molec. Phys.*, **69**, 803.

[26] Hohm, U., and Kerl, K., 1990, *Molec. Phys.*, **69**, 819.

[27] Hohm, U., and Kerl, K., 1986, *Molec. Phys.*, **58**, 541.

[28] Kerl, K., and Häusler, H., 1984, *Ber. Bunsenges. Phys. Chem.*, **88**, 992.

[29] Bogaard, M. P., Buckingham, A. D., Pierens, R. K., and White, A. H., 1978, *J. Chem. Soc. Faraday Trans. I*, **74**, 3008.

[30] Monan, M., Bribes, J.-L., and Gaufrès, R., 1982, *J. Raman. Spectrosc.*, **12**, 190.

[31] Murphy, W. F., 1977, *J. chem. Phys.*, **67**, 5877.

[32] Buckingham, A. D., 1955, *Proc. Phys. Soc. A*, **68**, 910.

[33] Buckingham, A. D., and Pople, J. A., 1955, *Proc. Phys. Soc. A*, **68**, 905.

[34] Buckingham, A. D., 1976, *J. chem. Phys.*, **64**, 364.

[35] Tammer, R., and Hüttner, W., 1994, *Molec. Phys.*, **83**, 579.

[36] Buckingham, A. D., and Disch, R. L., 1963, *Proc. R. Soc. Lond. A*, **273**, 275.

[37] Buckingham, A. D., Graham, C., and Williams, J. H., 1983, *Molec. Phys.*, **49**, 703.

[38] Imrie, D. A., and Raab, R. E., 1991, *Molec. Phys.*, **74**, 833.

[39] Watson, J. N., 1995, PhD Thesis, University of New England, Armidale NSW, Australia.

[40] Coonan, M. H., and Ritchie, G. L. D., 1993, *Chem. Phys. Lett.*, **202**, 237.

[41] Coonan, M. H., 1995, PhD Thesis, University of New England, Armidale NSW, Australia.

[42] Kling, H., Geschka, H., and Hüttner, W., 1983, *Chem. Phys. Lett.*, **96**, 631.

[43] Tanaka, K., Ito, H., Harada, K., and Tanaka, T., 1984, *J. chem. Phys.*, **80**, 5893.

[44] Tanaka, K., Ito, H., and Tanaka, T., 1987, *J. chem. Phys.*, **87**, 1557.

[45] Ellenbroek, A. W., and Dymanus, A., 1978, *Chem. Phys.*, **35**, 227.

[46] Flygare, W. H., and Benson, R. C., 1971, *Molec. Phys.*, **20**, 225.

[47] Kukolich, S. G., and Casleton, K. H., 1973, *Chem. Phys. Lett.*, **18**, 408.

[48] Norris, C. L., Pearson, E. F., and Flygare, W. H., 1974, *J. chem. Phys.*, **60**, 1758.

[49] Sutter, D. H., and Flygare, W. H., 1976, *Top. Curr. Chem.*, **63**, 89.

[50] Majer, W., Lutzmann, P., and Hüttner, W., 1994, *Molec. Phys.*, **83**, 567.

[51] Barnes, J. A., Gough, T. E., and Stoer, M., 1995, *Chem. Phys. Lett.*, **237**, 437.

[52] Bass, S. M., DeLeon, R. L., and Muenter, J. S., 1987, *J. chem. Phys.*, **86**, 4305.

[53] Bishop, D. M., Lam, B., and Epstein, S. T., 1988, *J. chem. Phys.*, **88**, 337.

[54] Buckingham, A. D., and Stephens, P. J., 1963, *Molec. Phys.*, **7**, 481.

[55] Chen, Y.-T., and Oka, T., 1988, *J. chem. Phys.*, **88**, 5282.

[56] Gough, T. E., Orr, B. J., and Scoles, G., 1983, *J. molec. Spec.*, **99**, 143.

[57] Buckingham, A. D., and Pople, J. A., 1955, *Trans. Faraday Soc.*, **51**, 1029.

[58] Watson, H. E., 1927, *Proc. R. Soc. Lond. A*, **117**, 43.

[59] Smyth, C. P., and Zahn, C. T., 1925, *J. Am. Chem. Soc.*, **47**, 2501.

[60] Bogaard, M. P., Buckingham, A. D., and Ritchie, G. L. D., 1982, *Chem. Phys. Lett.*, **90**, 183.

[61] Burnham, A. K., Buxton, L. W., and Flygare, W. H., 1977, *J. chem. Phys.*, **67**, 4990.

[62] Amos, R. D., Alberts, I. L., Andrews, J. S., Colwell, S. M., Handy, N. C., Jayatilaka, D., Knowles, P. J., Kobayashi, R., Noga, N., Laidig, K. E., Maslen, P. E., Murray, C. W., Rice, J. E., Sanz, J. E., Simandiras, E. D., Stone, A. J., and Su, M.-D., 1994, CADPAC: The Cambridge Analytic Derivatives Package, issue 5.2.

[63] Frisch, M. J., Trucks, G. W., Schlegel, H. B., Gill, P. M. W., Johnson, B. G., Robb, M. A., Cheeseman, J. R., Keith, T., Petersson, G. A., Montgomery, J. A., Raghavachari, K., Al-Laham, M. A., Zakrzewski, V. G., Ortiz, J. V., Foresman, J. B., Peng, C. Y., Ayala, P. Y., Chen, W., Wong, M. W., Andres, J. L., Replogle, E. S., Gomperts, R., Martin, R. L., Fox, D. J., Binkley, J. S., Defrees, D. J., Baker, J., Stewart, J. P., Head-Gordon, M., Gonzalez, C., and Pople, J. A., 1995, Gaussian 94.

[64] Schmidt, M. W., Baldridge, K. K., Boatz, J. A., Elbert, S. T., Gordon, M. S., Jensen, J. H., Koseki, S., Matsunaga, N., Nguyen, K. A., Su, S. J., Windus, T. L., Dupuis, M., and Montgomery, J. A., 1993, *J. Comp. Chem.*, **14**, 1347.

[65] Levine, I. N., 1991, *Quantum Chemistry* (Prentice Hall, New Jersey).

[66] McQuarrie, D. A., 1973, *Statistical Thermodynamics* (Harper and Row).

[67] Giacovazzo, C., Monaco, H. L., Viterbo, D., Scordari, F., Gilli, G., Zanotti, G., and Catti, M., 1992, *Fundamentals of Crystallography* (IUCr, Oxford Science Publications).

[68] Graner, G., 1992, In *Accurate Molecular Structures. Their Determination and Importance*, Vol. 1, edited by A. Domenicano and I. Hargittai (IUCr, Oxford University Press), p. 65.

[69] Hargittai, I., 1992, In *Accurate Molecular Structures. Their Determination and Importance*, Vol. 1, edited by A. Domenicano and I. Hargittai (IUCr, Oxford University Press), p. 270.

[70] Maitland, G. C., Rigby, M., Smith, E. B., and Wakeham, W. A., 1981, *Intermolecular Forces* (Oxford University Press).

[71] Levine, I. N., 1975, *Molecular Spectroscopy* (Wiley, New York).

[72] Wilson, E. B., Decius, J. C., and Cross, P. C., 1955, *Molecular Vibrations. The theory of infrared and Raman vibrational spectra* (McGraw-Hill).

[73] Raynes, W. T., Lazzeretti, P., and Zanasi, R., 1988, *Molec. Phys.*, **64**, 1061.

[74] Raynes, W. T., Fowler, P. W., Lazzeretti, P., Zanasi, R., and Grayson, M., 1988, *Molec. Phys.*, **64**, 143.

[75] Wong, A. T., Bacskay, G. B., Hush, N. S., and Bogaard, M. P., 1991, *Molec. Phys.*, **74**, 1037.

[76] Martí, J., Andrés, J. L., Bertrán, J., and Duran, M., 1993, *Molec. Phys.*, **80**, 625.

[77] Werner, H.-J., and Meyer, W., 1976, *Molec. Phys.*, **31**, 855.

[78] Spirko, V., Jensen, H. J. A., and Jørgensen, P., 1990, *Chem. Phys.*, **144**, 343.

[79] Wormer, P. E. S., Olthof, E. H. T., Engeln, R. A. H., and Reuss, J., 1993, *Chem. Phys.*, **178**, 189.

[80] Fowler, P. W., Riley, G., and Raynes, W. T., 1981, *Molec. Phys.*, **42**, 1463.

[81] Fowler, P. W., and Raynes, W. T., 1982, *Molec. Phys.*, **45**, 667.

[82] Riley, G., Raynes, W. T., and Fowler, P. W., 1979, *Molec. Phys.*, **38**, 877.

[83] Cohen, M. J., Willetts, A., Amos, R. D., and Handy, N. C., 1994, *J. chem. Phys.*, **100**, 4467.

[84] Bishop, D. M., Kirtman, B., Kurtz, H. A., and Rice, J. E., 1993, *J. chem. Phys.*, **98**, 8024.

[85] Lindh, R., and Liu, B., 1991, *J. chem. Phys.*, **94**, 4356.

[86] Cernusak, I., Diercksen, G. H. F., and Sadlej, A. J., 1986, *Chem. Phys.*, **108**, 45.

[87] Bishop, D. M., and Cybulski, S. M., 1994, *J. chem. Phys.*, **101**, 2180.

[88] Archibong, E. F., and Thakkar, A. J., 1993, *Chem. Phys. Lett.*, **201**, 485.

[89] Adamowicz, L., and Bartlett, R. J., 1986, *J. chem. Phys.*, **84**, 4988.

[90] Malik, D. J., 1988, *J. chem. Phys.*, **88**, 2624.

[91] Malik, D. J., and Dykstra, C. E., 1985, *J. chem. Phys.*, **83**, 6307.

[92] Dykstra, C. E., and Malik, D. J., 1987, *J. chem. Phys.*, **87**, 2806.

[93] Buckingham, A. D., and Urland, W., 1975, *Chem. Rev.*, **75**, 113.

[94] Fowler, P. W., 1983, *Molec. Phys.*, **48**, 153.

[95] Fowler, P. W., and Raynes, W. T., 1981, *Molec. Phys.*, **43**, 65.

[96] Oddershede, J., Jørgensen, P., and Beebe, N. H. F., 1975, *J. chem. Phys.*, **63**, 2996.

[97] Nielsen, E. S., Jørgensen, P., and Oddershede, J., 1980, *J. chem. Phys.*, **73**, 6238.

[98] Rice, J. E., and Handy, N. C., 1991, *J. chem. Phys.*, **94**, 4959.

[99] Rice, J. E., Amos, R. D., Colwell, S. M., Handy, N. C., and Sanz, J., 1990, *J. chem. Phys.*, **93**, 8828.

[100] Kobayashi, R., Koch, H., and Jørgensen, P., 1994, *Chem. Phys. Lett.*, **219**, 30.

[101] Kobayashi, R., Amos, R. D., Koch, H., and Jørgensen, P., 1996, *Chem. Phys. Lett.*, **253**, 373.

[102] Bishop, D. M., 1994, *Adv. Quantum Chem.*, **25**, 1.

[103] Kirtman, B., and Bishop, D. M., 1990, *Chem. Phys. Lett.*, **175**, 601.

[104] Bishop, D. M., and Kirtman, B., 1991, *J. chem. Phys.*, **95**, 2646.

[105] Bishop, D. M., and Kirtman, B., 1992, *J. chem. Phys.*, **97**, 5255.

[106] Born, M., and Oppenheimer, J. R., 1927, *Ann. Phys.*, **84**, 457.

[107] Fowler, P. W., 1981, *Molec. Phys.*, **43**, 591.

[108] Fowler, P. W., 1984, *Molec. Phys.*, **51**, 1423.

[109] Alms, G. R., Burnham, A. K., and Flygare, W. H., 1975, *J. chem. Phys.*, **63**, 3321.

Chapter Two

Theory

2.1 Vibrational and rotational motion

The time-independent Schrödinger equation is

$$H(\boldsymbol{r};\boldsymbol{R})\psi(\boldsymbol{r};\boldsymbol{R}) = E(\boldsymbol{R})\psi(\boldsymbol{r};\boldsymbol{R}) \tag{2.1}$$

where $E(\boldsymbol{R})$ represents the energy eigenvalues of the system, $\psi(\boldsymbol{r};\ \boldsymbol{R})$ the eigenfunctions. The total molecular Hamiltonian operator, $H(\boldsymbol{r};\ \boldsymbol{R})$, involves electronic coordinates $\boldsymbol{r}$ and nuclear coordinates $\boldsymbol{R}$ for a system of N nuclei and n electrons, and is given in Bohr atomic units by

$$\begin{aligned} H(\boldsymbol{r};\boldsymbol{R}) &= T_n + T_e + V_{nn} + V_{ne} + V_{ee} \\ &= -\frac{1}{2}\sum_{a}^{N}\frac{\nabla_a^2}{M_a} - \frac{1}{2}\sum_{i}^{n}\frac{\nabla_i^2}{m_i} + \sum_{a<b}^{N}\frac{Z_a Z_b e^2}{|\boldsymbol{R}_a - \boldsymbol{R}_b|} - \sum_{a,i}^{N,n}\frac{Z_a e^2}{|\boldsymbol{r}_i - \boldsymbol{R}_a|} + \sum_{i<j}^{n}\frac{e^2}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} \end{aligned} \tag{2.2}$$

where T_n is the kinetic energy of the nuclei, T_e the kinetic energy of the electrons, V_{nn} the nuclear repulsion energy, V_{ne} the nuclear-electron attraction energy and V_{ee} the electron-electron repulsion energy. The letters (a, b) and (i, j) are summation indices over the nuclei and electrons respectively. Solution of (2.1) using the full molecular Hamiltonian is an extremely complicated task. In order to simplify the problem, the Born-Oppenheimer approximation [1] is usually invoked, utilising the fact that the mass of an electron is very much less than the mass of a nucleus, thereby acknowledging that electronic motion occurs much faster than nuclear motion. The nuclear kinetic energy term T_n then vanishes from the above Hamiltonian leading to the Born-Oppenheimer Hamiltonian, where the nuclear positions enter into the equations as parameters and not as variables. The electronic part of the equation may then be solved for fixed values of $\boldsymbol{R}$, and in doing so the concept of a

Born-Oppenheimer potential energy (hyper)surface naturally arises. The electronic part of the wavefunction may be solved by various methods such as the self consistent field (SCF) approximation [2], density functional theory (DFT) [3] or other approximate methods that involve treatment of electron correlation such as Møller-Plesset perturbation theory [4] or coupled cluster theory [5]. The potential energy surface obtained from the electronic solution defines the motion of the nuclei and therefore, with the use of the potential surface, the nuclear part of the time-independent Schrödinger equation may also be solved. The Hamiltonian for the nuclear motion can be expressed as [6]

$$H = \frac{1}{2}\sum_{\alpha\beta}(J_\alpha - \pi_\alpha)\mu_{\alpha\beta}(J_\beta - \pi_\beta) + \frac{1}{2}\sum_k P_k^2 - \frac{1}{8}\hbar^2\sum_\alpha \mu_{\alpha\alpha} + V(Q) \tag{2.3}$$

where J_α are the components of total angular momentum, π_α are the vibrational angular momenta, $\mu_{\alpha\beta}$ is the inverse of the modified moment of inertia matrix, P_k are the nuclear vibrational momenta and the Born-Oppenheimer potential $V(Q)$ is a function of $3N$–6 vibrational coordinates Q_k for N nuclei ($3N$–5 for a linear molecule). Summation subscripts in this section reserve the letters $i, j = 1, 2, ..., N$ for sums over the atoms, and the letters $k, l, m, n = 1, 2, ..., 3N$–6 ($3N$–5 for a linear molecule) for vibrational coordinates. The third term in the above equation is often neglected since it is of the same order of magnitude as the terms ignored by the Born-Oppenheimer approximation. The above Hamiltonian has been derived from the space-fixed cartesian axis Hamiltonian by separating out the translational coordinates by referring the nuclei to the centre of mass, and separating out the rotational coordinates by using a molecule-fixed axis system specified by Euler angles. Instantaneous positions of the atoms may then be defined by the set of cartesian displacement vectors $r_{\alpha i} - r_{\alpha i}^e$. An orthogonal transformation of the $3N$ mass-weighted displacements $m_i^{\frac{1}{2}}(r_{\alpha i} - r_{\alpha i}^e)$ leads to a set of $3N$ normal coordinates, consisting of $3N$–6 vibrational coordinates Q_k, three translational coordinates T_α and three rotational coordinates R_α defined by the equations

$$Q_k = \sum_i l_{\alpha i}^k m_i^{\frac{1}{2}}(r_{\alpha i} - r_{\alpha i}^e) \tag{2.4}$$

$$T_\alpha = M^{-\frac{1}{2}} \sum_i m_i^{\frac{1}{2}} \left[m_i^{\frac{1}{2}} \left(r_{\alpha i} - r_{\alpha i}^e \right) \right] \tag{2.5}$$

$$R_\alpha = \left(I_{\alpha\beta}^e \right)^{-\frac{1}{2}} \sum_i m_i^{\frac{1}{2}} e_{\beta\gamma\delta} r_{\gamma i}^e \left(r_{\delta i} - r_{\delta i}^e \right) \tag{2.6}$$

where m_i is the mass of the ith nucleus, $l_{\alpha i}^k$ ($\boldsymbol{l}$ matrix) are the eigenvectors of the mass-weighted cartesian force constant matrix and $r_{\alpha i} - r_{\alpha i}^e$ is the cartesian displacement from the equilibrium nuclear configuration, M is the total molecular mass, $I_{\alpha\beta}^e$ is the inertia tensor at the equilibrium nuclear configuration and $e_{\alpha\beta\gamma}$ is the unit antisymmetric tensor in three dimensions. Vibrational coordinates are chosen to diagonalize the second derivatives of the potential $V(Q)$, and this is conveniently carried out using the cartesian second derivatives of the energy, $f_{\alpha i \beta j}$, that are mass-weighted and diagonalized using the equation,

$$\left(l_{\alpha i}^k \right)^{-1} \left[\frac{f_{\alpha i \beta j}}{\sqrt{m_i m_j}} \right] \left(l_{\beta j}^l \right) = \delta_{kl} \left(4\pi^2 c^2 \omega_k^2 \right) \tag{2.7}$$

to obtain the $\boldsymbol{l}$ matrix from the eigenvectors and the harmonic vibrational frequencies, ω_k, from the eigenvalues. It is desirable for the molecule-fixed axis system to achieve maximum separation between vibrational and rotational motion. The Eckart conditions [7] offer one way of achieving this separation by minimising the vibrational angular momenta and this amounts to setting $T_\alpha = R_\alpha = 0$. Using the definition of the normal coordinates, the terms in the vibration-rotation Hamiltonian are given as [6]

$$\pi_\alpha = \sum_{kl} \zeta_{kl}^\alpha Q_k P_l \tag{2.8}$$

$$P_k = -i\hbar \frac{\partial}{\partial Q_k} \tag{2.9}$$

$$\mu_{\alpha\beta} = \left[I_{\alpha\beta} - \sum_{k,l,m} \zeta_{km}^\alpha \zeta_{lm}^\beta Q_k Q_l \right]^{-1} \tag{2.10}$$

$$\zeta_{kl}^\alpha = -\zeta_{lk}^\alpha = e_{\alpha\beta\gamma} \sum_i l_{\beta i}^k l_{\gamma i}^l \tag{2.11}$$

$$I_{\alpha\beta} = e_{\alpha\gamma\varepsilon} e_{\beta\delta\varepsilon} \sum_i m_i r_{\gamma i} r_{\delta i} \tag{2.12}$$

The potential energy, V, may be expressed as a Taylor series expansion about the potential energy minimum, in terms of the normal coordinates

$$V = V_e + \frac{1}{2}\sum_k \lambda_k Q_k^2 + \frac{1}{6}\sum_{k,l,m} \Phi_{klm} Q_k Q_l Q_m + \frac{1}{24}\sum_{k,l,m,n} \Phi_{klmn} Q_k Q_l Q_m Q_n + \ldots \tag{2.13}$$

where V_e is the energy at the potential energy minimum, and λ_k, Φ_{klm}, Φ_{klmn} are the partial second, third and fourth derivatives with respect to the normal coordinates. Similarly, the moment of inertia tensor $I_{\alpha\beta}$ may also be written in this manner, truncated at quadratic terms, as

$$I_{\alpha\beta} = I^e_{\alpha\beta} + \frac{1}{2}\sum_k a_k^{\alpha\beta} Q_k + \frac{1}{4}\sum_{k,l}\left(\frac{a_k^{\alpha\gamma} a_l^{\delta\beta}}{I^e_{\gamma\delta}}\right) Q_k Q_l + \ldots \tag{2.14}$$

where the partial first derivative of the inertia tensor is

$$a_k^{\alpha\beta} = \left(\frac{\partial I_{\alpha\beta}}{\partial Q_k}\right)_e = 2 e_{\alpha\gamma\varepsilon} e_{\beta\delta\varepsilon} \sum_i m_i^{\frac{1}{2}} r^e_{\gamma i} l^k_{\delta i} \tag{2.15}$$

A set of dimensionless normal coordinates, q, are defined such that [8]

$$q_k = \gamma^{\frac{1}{2}} Q_k = \left(\frac{4\pi^2 c\omega_k}{h}\right)^{\frac{1}{2}} Q_k = \left(\frac{\lambda_k^{\frac{1}{2}}}{\hbar}\right)^{\frac{1}{2}} Q_k \tag{2.16}$$

where ω_k is the harmonic vibrational frequency for the kth mode in units of cm^{-1}. The potential energy, V, is expanded in a Taylor series of the dimensionless normal coordinates, q_k, about the potential energy minimum, to yield

$$V = V_e + \frac{1}{2}\sum_k \omega_k q_k^2 + \frac{1}{6}\sum_{k,l,m} \phi_{klm} q_k q_l q_m + \frac{1}{24}\sum_{k,l,m,n} \phi_{klmn} q_k q_l q_m q_n + \ldots \tag{2.17}$$

where V_e is the energy at the potential energy minimum and ϕ_{klm} and ϕ_{klmn} are the cubic and quartic force constants respectively defined by

$$\phi_{klm} = \left(\frac{\partial^3 V}{\partial q_k \partial q_l \partial q_m} \right)_e \tag{2.18}$$

$$\phi_{klmn} = \left(\frac{\partial^4 V}{\partial q_k \partial q_l \partial q_m \partial q_n} \right)_e \tag{2.19}$$

and are evaluated at the potential energy minimum or r_e geometry. Expanding the inverse moment of inertia tensor in a similar way [9] leads to

$$\frac{\mu_{\alpha\beta}}{2} = B_\alpha \delta_{\alpha\beta} + \sum_k B_k^{\alpha\beta} q_k + \frac{3}{8B_\gamma} \sum_{k,l} \left(B_k^{\alpha\gamma} B_l^{\gamma\beta} + B_l^{\alpha\gamma} B_k^{\gamma\beta} \right) q_k q_l + \ldots \tag{2.20}$$

where the rotational constants and the first-derivatives of the rotational constants with respect to dimensionless normal coordinates are defined as

$$B_\alpha = \frac{\hbar^2}{2hc} \frac{1}{I_{\alpha\alpha}^e} \tag{2.21}$$

$$B_k^{\alpha\beta} = \frac{\hbar^2}{2hc} \frac{a_k^{\alpha\beta}}{I_{\alpha\alpha}^e I_{\beta\beta}^e} \tag{2.22}$$

The nuclear motion Hamiltonian is then greatly simplified and is expressed in powers of the vibrational and rotational operators [9],

$$H = H_{20} + H_{02} + \lambda(H_{30} + H_{21} + H_{12}) + \lambda^2(H_{40} + H_{22}) \tag{2.23}$$

$$H_{20} = \frac{1}{2} \sum_r \omega_r (p_r^2 + q_r^2)$$

$$H_{02} = \sum_\alpha B_\alpha J_\alpha^2$$

$$\lambda H_{30} = \frac{1}{6} \sum_{k,l,m} \phi_{klm} q_k q_l q_m$$

$$\lambda H_{12} = \sum_k B_k^{\alpha\beta} q_k J_\alpha J_\beta$$

$$\lambda^2 H_{40} = \frac{1}{24} \sum_{k,l,m,n} \phi_{klmn} q_k q_l q_m q_n + B_\alpha \pi_\alpha^2$$

$$\lambda^2 H_{22} = \frac{3}{8B_\gamma} \sum_{k,l} \left(B_k^{\alpha\gamma} B_l^{\gamma\beta} + B_l^{\alpha\gamma} B_k^{\gamma\beta} \right) q_k q_l J_\alpha J_\beta$$

Zeroth-order terms H_{20} and H_{02} are the harmonic oscillator rigid-rotor parts of the vibrational Hamiltonian. First-order terms include H_{30}, which accounts for cubic anharmonicity of the potential, H_{21} describing the Coriolis interaction between the vibrational angular momentum and the total angular momentum and H_{12} describing centrifugal distortion. Second-order terms shown here include H_{40} which is the quartic anharmonicity of the potential energy and H_{22} which describes the vibrational dependence of the rotational energies. The method of grouping the terms in the Hamiltonian is not unique and several different partitioning methods have been proposed. Generally, the grouping scheme depends on the problem under investigation; the Nielsen classification scheme [10], outlined above, is most often used in infrared spectroscopy, where the H_{20} and H_{02} terms are tied together in the zeroth-order term. The terms are grouped in this way to facilitate perturbation theory solutions of the nuclear Schrödinger equation with the contact transformation method.

Contact transformation theory is a method of perturbation theory that utilises a unitary transformation of the vibration-rotation Hamiltonian to give an effective Hamiltonian which is diagonal, up to a desired order, in the zeroth order basis states. The exact kth state is related to the kth zeroth-order state, k^0, via the equation

$$|k\rangle = \mathrm{e}^{\mathrm{i}\lambda S}|k^0\rangle \tag{2.24}$$

where S is an hermitian operator termed the contact transformation operator and λ is a perturbation parameter with a value between 0 and 1. Hamiltonian matrix elements in the exact basis are related to the effective Hamiltonian matrix elements in the zeroth-order basis by

$$\langle a|H|k\rangle = \langle a^0|\mathrm{e}^{-\mathrm{i}\lambda S}H\mathrm{e}^{\mathrm{i}\lambda S}|k^0\rangle = \langle a^0|\tilde{H}|k^0\rangle \tag{2.25}$$

An expansion of the exponential of the contact transformation operator, exp (iλS), leads to an effective Hamiltonian

$$\tilde{H} = H_0 + \lambda\tilde{H}_1 + \lambda^2\tilde{H}_2 + \ldots \tag{2.26}$$

where

$$\tilde{H}_1 = H_1 + \mathrm{i}[S_1, H_0]$$

$$\tilde{H}_2 = H_2 + \mathrm{i}[S_1, H_1] - \frac{1}{2}[S_1,[S_1, H_0]] + \mathrm{i}[S_2, H_0]$$

and the contact transformation operator, S, is

$$S = \lambda S_1 + \lambda^2 S_2 + \ldots$$

The perturbation problem then essentially consists of evaluating the matrix elements of the commutator relations in the zeroth-order basis using a known formula for S [10].

Through the use of second-order contact transformation theory, the vibrational energy levels for a symmetric top are [11-13]

$$\begin{aligned} G(\upsilon, l) = & \sum_s \omega_s(\upsilon_s + \tfrac{1}{2}) + \sum_t \omega_t(\upsilon_t + 1) + \sum_{s \le s'} X_{ss'}(\upsilon_s + \tfrac{1}{2})(\upsilon_{s'} + \tfrac{1}{2}) \\ & + \sum_{s,t} X_{st}(\upsilon_s + \tfrac{1}{2})(\upsilon_t + 1) + \sum_{t \le t'} X_{tt'}(\upsilon_t + 1)(\upsilon_{t'} + 1) + \sum_{t \le t'} G_{tt'} l_t l_{t'} \end{aligned} \tag{2.27}$$

where υ_i are the vibrational quantum numbers for a particular vibrational state and l_t is the vibrational angular momentum quantum number which may take the values

$$l_t = \pm\upsilon_t,\ \pm(\upsilon_t - 2),\ \ldots,\ \pm 1 \text{ or } 0$$

In these equations, and those of the following section, the subscripts s, s' and t, t' label non-degenerate and degenerate modes respectively. Equations for the coefficients $X_{ss'}$, X_{st}, $X_{tt'}$ and $G_{tt'}$ in terms of harmonic frequencies, cubic and quartic force constants and other known spectroscopic parameters, are given in Willetts and Handy [12]. Fundamental vibrational frequencies are then calculated from G (υ_k = 1, l_k) − G (0, 0) in equation (2.27) and the explicit form of the fundamental vibrational frequencies, ν_k, is

$$\nu_k = \omega_k + 2X_{kk} + \frac{g_k}{2}\sum_{l,k \le l} X_{kl} + \frac{1}{2}\sum_r X_{kr} + (g_k - 1)G_{kk} l_k^2 \tag{2.28}$$

where g_k is the degeneracy of the kth mode. The above equations reduce to those of an asymmetric top if degenerate modes are deleted and to the diatomic case for a single mode. Equations for the vibrational energy levels of spherical tops have been presented by Hecht [14] and Hodgkinson *et al.* [15] and will not be presented here. Instead, the theory for the corresponding vibrational and rotational levels of a general property is described.

2.2 Vibrational and rotational effects on molecular properties

In a similar vein to a potential energy surface that results from the Born-Oppenheimer approximation, derivatives of the energy with respect to external perturbations such as external electric fields and field-gradients give rise to the concept of a property (hyper)surface. The property surface, $P(\boldsymbol{R})$, related to an operator P is defined as the expectation value of the operator over the electronic wavefunction,

$$P(\boldsymbol{R}) = \int \Psi^{el*}(\boldsymbol{r};\boldsymbol{R}) P(\boldsymbol{r};\boldsymbol{R})\, \Psi^{el}(\boldsymbol{r};\boldsymbol{R})\, d\boldsymbol{r} \tag{2.29}$$

where the property surface $P(\boldsymbol{R})$ is a function that depends only on the nuclear coordinates $\boldsymbol{R}$. To simplify the notation, the property surface $P(\boldsymbol{R})$ is referred to simply as P or $\hat{P}$ and may be expanded in a Taylor series of the general nuclear coordinates, $\boldsymbol{R}_i$, about the potential energy minimum as

$$P = P_e + \sum_i P_i \boldsymbol{R}_i + \frac{1}{2}\sum_{i,j} P_{ij}\boldsymbol{R}_i\boldsymbol{R}_j + \frac{1}{6}\sum_{i,j,k} P_{ijk}\boldsymbol{R}_i\boldsymbol{R}_j\boldsymbol{R}_k + \frac{1}{24}\sum_{i,j,k,l} P_{ijkl}\boldsymbol{R}_i\boldsymbol{R}_j\boldsymbol{R}_k\boldsymbol{R}_l + \ldots \tag{2.30}$$

where suitable choices of nuclear coordinates $\boldsymbol{R}_i$ include curvilinear internal coordinates ($\mathcal{R}_i$), cartesian coordinates ($X_{\alpha i}$), symmetry internal coordinates (S_i), normal coordinates (Q_i) and dimensionless normal coordinates (q_i). Property surfaces may be used to obtain infrared and Raman intensities if P is the dipole moment and polarizability respectively [16, 17], the properties in arbitrary vibrational-rotational states [18-21], along with the effects of isotopic substitution [22, 23] and temperature [24-26] on molecular properties. A more recent and novel application of property derivatives relates to the vibrational Stark effect and the effect of electric fields on infrared and Raman spectra [27, 28].

If the molecular properties are time-symmetric, as is the case for most properties including electric dipole and quadrupole moments and polarizabilities, then the above

equation (2.30) is valid. However, for properties that are antisymmetric with respect to time, such as those involving complex or imaginary number quantities, a property surface defined with terms in odd powers of the nuclear velocities, $\dot{\boldsymbol{R}}$, is required [29]. Vibrational circular dichroism (VCD) [30], the differential absorption of left and right circularly polarized light close to the vibrational frequencies of a molecule, is one such application where velocity derivatives can be utilised [29].

The expectation value of a general property surface P, for an arbitrary rotational-vibrational state (vibrational average) specified by a set of quantum numbers k is

$$\langle P \rangle_k = \langle k | P | k \rangle = \int \psi_k^* \hat{P} \psi_k \, \mathrm{d}\tau \tag{2.31}$$

which relates the normalised vibrational-rotational wavefunction, ψ_k, and its complex conjugate, ψ_k^*, to the quantum mechanical operator of the electrical property, $\hat{P}$. Integration over all dimensionless normal coordinates and Euler angles, $\mathrm{d}\tau$, for the vibrational-rotational quantum states, k, is then performed.

Commonly, the equation for a property in an arbitrary vibrational-rotational level is used for calculation of a property zero-point vibrational correction (ZPVC), defined as the difference between the rotationless vibrational ground state property and the property at the equilibrium nuclear configuration,

$$\mathrm{ZPVC} = \langle P \rangle_0 - P_e \tag{2.32}$$

The ZPVC is a correction for the effects of zero-point vibrational motion on the property and may be regarded as a first step towards correcting electronic properties for the effects of vibrational motion. Zero-point vibrational motion is present even at absolute zero (0 K) and so the correction should be necessary for almost all accurate theoretical predictions of experimental molecular properties. The majority of experiments are carried out at room temperatures so that the largest proportion of molecules reside in their ground vibrational states with a smaller proportion populating excited vibrational states. Rotational corrections to a property at room temperatures from excited rotational states are also expected to be negligible when compared to the ZPVC. For state specific properties, such as dipole and quadrupole moments from molecular beam experiments [31-33], the property in a given vibrational-rotational state may also be calculated.

There are essentially two ways of solving the integral equation (2.31), both of which have particular advantages and disadvantages. The first is based on direct evaluation of the integral with vibrational wavefunctions and the second method, which is favoured in the present thesis, centres on a perturbation theory approach. The two methods are outlined in the following sections.

2.2.1 *Variational methods*

One way of solving the integral equation is to utilise variational methods [16, 34-38] to calculate the vibrational wavefunction. For a diatomic molecule, the Numerov-Cooley method [39, 40] and the derivative Numerov-Cooley method [41, 42] have been used for this purpose and involve computation of the potential energy and property curves for the diatomic molecule followed by numerical integration schemes. The Numerov-Cooley should provide exact vibrational wavefunctions for the given potential energy surface, unlike approximate perturbation theory methods that depend on orders of the perturbation. Unfortunately, the Numerov-Cooley method cannot be generalised to polyatomic molecules. Solution of the integral equation for a polyatomic molecule usually requires the anharmonic states to be expanded in a basis made up from products of harmonic oscillator wavefunctions [16]. An anharmonic potential in the dimensionless normal coordinates is used with integrals of various powers of the dimensionless normal coordinates, extracted from tables such as those of Wilson, Decius and Cross [43]. The Hamiltonian matrix is then constructed and diagonalized to yield the energy values (eigenvalues) and the corresponding anharmonic vibrational states in terms of the harmonic oscillator basis functions (eigenvectors). Calculation of matrix elements of the property surface involving harmonic oscillator wavefunctions is then carried out, followed by a unitary two-index transformation of the property matrix with the eigenvectors [16]. The variational method shows particular promise, as not only the expectation values of the property in the set of basis states are obtained but also the transition matrix elements linking particular vibrational states. This would naturally lead to calculation of transition intensities for infrared and Raman spectra if the property is the dipole moment and polarizability, respectively. Variational methods also possess the added advantage that resonance is also treated exactly since the Hamiltonian matrix is explicitly diagonalized in a similar way to degenerate perturbation theory [2, 44]. Variational methods are generally more accurate than those based upon perturbation theory because the equivalent level of perturbation theory reached by variational procedures is

dependent upon the number of vibrational state configurations included in the Hamiltonian matrix. The primary disadvantage of the variational method is the high computational cost of the procedure for molecules with more than four atoms since the number of basis states required for a second-order variational-perturbation treatment is roughly proportional to N^6 for N vibrational modes. Molecular symmetry can be exploited to break the Hamiltonian matrix into smaller symmetry blocks for diagonalization of the huge matrices involved. Special diagonalization procedures such as those based on the Lanczos method [45] may be required for this purpose.

2.2.2 *Perturbation theory expressions*

The second method requires the use of perturbation theory or contact transformation theory to obtain an analytical expression for the property expectation value integral equation. A zeroth-order basis constructed from products of harmonic oscillator functions and symmetric top rigid rotor wavefunctions is utilised for the purpose. Perturbation theory methods for molecular properties allow straightforward generalisation to larger molecules, and are widely favoured over variational methods for polyatomic molecules due to low computational cost after implementation of the necessary formulae. For these reasons, the perturbation theory approach is used exclusively in the present thesis. Perturbation theory expressions for the value of a geometry-dependent property in an arbitrary rotational-vibrational state have been derived by Fowler [19] for symmetric tops and linear molecules and, in order to clearly display the connection between the energy [12, 13] and property cases, the relevant equations have been expressed here in a slightly different form. Expanding any geometry-dependent property P in a Taylor series of the dimensionless normal coordinates about the potential energy minimum

$$P = P_e + \sum_i P_i q_i + \frac{1}{2}\sum_{i,j} P_{ij} q_i q_j + \frac{1}{6}\sum_{i,j,k} P_{ijk} q_i q_j q_k + \frac{1}{24}\sum_{i,j,k,l} P_{ijkl} q_i q_j q_k q_l + \ldots \qquad (2.33)$$

where P_e is the property at the potential energy minimum and P_i, P_{ij}, P_{ijk}, and P_{ijkl}, are the respective first, second, third and fourth derivatives of the property with respect to dimensionless normal coordinates (synonymous with linear, quadratic, cubic and quartic property derivatives). Utilising first-order contact transformation theory and the first-order terms in the vibration-rotation Hamiltonian in equation (2.23), the expectation value of the property in an arbitrary rotational-vibrational state may be derived and expressed as

$$\langle P\rangle_{vlJK} = P_e + P_0^{JK} + \sum_s A_s^{JK}(v_s+\tfrac{1}{2}) + \sum_t A_t^{JK}(v_t+1) + \sum_{s\le s'} B_{ss'}(v_s+\tfrac{1}{2})(v_{s'}+\tfrac{1}{2})$$
$$+ \sum_{s,t} B_{st}(v_s+\tfrac{1}{2})(v_t+1) + \sum_{t\le t'} B_{tt'}(v_t+1)(v_{t'}+1) + \sum_{t\le t'} G_{tt'}l_t l_{t'} \tag{2.34}$$

with the superscript JK denoting a rotational state dependence. The J and K dependence of P_0^{JK} , A_s^{JK} and A_t^{JK} are given by

$$P_0^{JK} = P_0 + P_J J(J+1) + P_K K^2 \tag{2.35}$$

$$A_s^{JK} = A_s + A_{sJ} J(J+1) + A_{sK} K^2 \tag{2.36}$$

$$A_t^{JK} = A_t + A_{tJ} J(J+1) + A_{tK} K^2 \tag{2.37}$$

and the coefficients in equations (2.34)-(2.37) are :

$$P_0 = \tfrac{1}{64}\sum_s P_{ssss} + \tfrac{1}{48}\sum_t P_{tttt} - \tfrac{7}{288}\sum_s\left(\frac{P_{sss}\phi_{sss}}{\omega_s}\right) + \tfrac{11}{72}\sum_t\left(\frac{P_{ttt}\phi_{ttt}}{\omega_t}\right)$$
$$+ \tfrac{3}{32}\sum_{s\ne s'} P_{sss'}\phi_{sss'}\Omega^{\#}_{ss'} + \tfrac{1}{8}\sum_{s,t} P_{stt}\phi_{stt}\Omega^{\#}_{ts} + \tfrac{1}{8}\sum_{t\ne t'}\left(\frac{P_{ttt'}\phi_{ttt'}}{\omega_{t'}}\right)\left(\frac{8\omega_t^2+\omega_{t'}^2}{4\omega_t^2-\omega_{t'}^2}\right) \tag{2.38}$$
$$- \sum_{t<t'} P_{stt'}\phi_{stt'}\Omega^{\#}_{stt'} + \sum_{t<t'<t''} P_{tt't''}\phi_{tt't''}\Omega^{\#}_{tt't''} - \sum_{s<s'<s''} P_{ss's''}\phi_{ss's''}\Omega^{\#}_{ss's''}$$

$$A_s = \frac{P_{ss}}{2} - \frac{1}{2}\sum_{s'}\frac{P_{s'}\phi_{sss'}}{\omega_{s'}} \tag{2.39}$$

$$A_t = \frac{P_{tt}}{2} - \frac{1}{2}\sum_{s}\frac{P_{s}\phi_{stt}}{\omega_{s}} \tag{2.40}$$

$$B_{ss} = \frac{P_{ssss}}{16} - \frac{1}{8}\sum_{s'} P_{sss'}\phi_{sss'}\Omega_{ss'} \tag{2.41}$$

$$B_{tt} = \frac{P_{tttt}}{16} - \frac{1}{8}\sum_{s} P_{stt}\phi_{stt}\Omega_{ts} - \frac{1}{8}\sum_{t'} P_{ttt'}\phi_{ttt'}\Omega_{tt'} \tag{2.42}$$

$$B_{ss'} = \frac{P_{sss's'}}{4} - \frac{1}{4}\sum_{s''}\frac{\left(P_{sss''}\phi_{s's's''} + P_{s's's''}\phi_{sss''}\right)}{\omega_{s''}} - \sum_{s''} P_{ss's''}\phi_{ss's''}\Omega_{ss's''} \tag{2.43}$$

$$B_{st} = \frac{P_{sstt}}{4} - \frac{1}{4}\sum_{s'}\frac{\left(P_{sss'}\phi_{s'tt} + P_{s'tt}\phi_{sss'}\right)}{\omega_{s'}} - \sum_{t'} P_{stt'}\phi_{stt'}\Omega_{stt'} \tag{2.44}$$

$$B_{tt'} = \frac{\left(P_{ttt'_a t'_a} + P_{ttt'_b t'_b}\right)}{8} - \frac{1}{4}\sum_s \frac{\left(P_{stt}\phi_{st't'} + P_{st't'}\phi_{stt}\right)}{\omega_s} - \frac{1}{2}\sum_s P_{stt'}\phi_{stt'}\Omega_{tt's} - \sum_{t''} P_{tt't''}\phi_{tt't''}\Omega_{tt't''} \tag{2.45}$$

$$G_{tt} = -\frac{P_{tttt}}{48} - \frac{1}{8}\sum_s P_{stt}\phi_{stt}\Omega^{\#}_{ts} + \frac{1}{8}\sum_{t'}\left(\frac{P_{ttt'}\phi_{ttt'}}{\omega_{t'}}\right)\left(\frac{8\omega_t^2 - \omega_{t'}^2}{4\omega_t^2 - \omega_{t'}^2}\right) \tag{2.46}$$

$$G_{tt'} = \sum_s P_{stt'}\phi_{stt'}\Omega^{\#}_{stt'} - 2\sum_{t''} P_{tt't''}\phi_{tt't''}\Omega^{\#}_{tt't''} \tag{2.47}$$

where the frequency factors are defined to be

$$\Omega_{ij} = \frac{8\omega_i^2 - 3\omega_j^2}{\omega_j\left(4\omega_i^2 - \omega_j^2\right)} \qquad \Omega_{ijk} = \frac{\omega_k\left(\omega_k^2 - \omega_i^2 - \omega_j^2\right)}{D_{ijk}}$$

$$\Omega^{\#}_{ij} = \frac{\omega_j}{\left(4\omega_i^2 - \omega_j^2\right)} \qquad \Omega^{\#}_{ijk} = \frac{\omega_i\omega_j\omega_k}{D_{ijk}} \tag{2.48}$$

and D_{ijk} is defined by

$$D_{ijk} = \left(\omega_i + \omega_j + \omega_k\right)\left(\omega_i + \omega_j - \omega_k\right)\left(\omega_i - \omega_j + \omega_k\right)\left(\omega_i - \omega_j - \omega_k\right) \tag{2.49}$$

with the subscripts i, j, and k labelling both non-degenerate and degenerate modes. If the property P in the above equations is replaced by the potential energy V, and the terms in equations (2.38)-(2.47) that involve cubic force constants are halved and the Coriolis and rotational constant corrections added [12], then the anharmonic constants in equation (2.27) are obtained.

Frequency factors in equations (2.48) possess denominators that are based on sums and differences of harmonic vibrational frequencies. In the event that the denominators are small and close to zero, the contribution to the energy or property levels from the offending terms can become extremely large. These "resonance" effects are an indication of the breakdown of the perturbation theory expressions and the most common types of resonance are the Fermi Type I and II resonances, Coriolis resonances and Darling-Dennison resonances. Conditions for occurrence of particular resonances are :

$2\omega_i \approx \omega_j$	and $\phi_{iij} \neq 0$	Fermi Type I
$\omega_i + \omega_j \approx \omega_k$	and $\phi_{ijk} \neq 0$	Fermi Type II
$2\omega_i \approx 2\omega_j$		Darling-Dennison
$\omega_i \approx \omega_j$	and $\zeta_{ij} \neq 0$.	Coriolis

The frequency factors in equation (2.48) can be factored [13] using partial fractions such that

$$\Omega_{ij} = \frac{1}{2}\left(\frac{1}{2\omega_i + \omega_j} - \frac{1}{2\omega_i - \omega_j} + \frac{4}{\omega_i}\right) \tag{2.50}$$

$$\Omega_{ij}^{\#} = -\frac{1}{2}\left(\frac{1}{2\omega_i + \omega_j} - \frac{1}{2\omega_i - \omega_j}\right) \tag{2.51}$$

$$\Omega_{ijk} = \frac{1}{4}\left(\frac{1}{\omega_i + \omega_j + \omega_k} - \frac{1}{\omega_i + \omega_j - \omega_k} + \frac{1}{\omega_i - \omega_j + \omega_k} - \frac{1}{\omega_i - \omega_j - \omega_k}\right) \tag{2.52}$$

$$\Omega_{ijk}^{\#} = \frac{1}{8}\left(\frac{1}{\omega_i + \omega_j + \omega_k} - \frac{1}{\omega_i + \omega_j - \omega_k} - \frac{1}{\omega_i - \omega_j + \omega_k} + \frac{1}{\omega_i - \omega_j - \omega_k}\right) \tag{2.53}$$

If the conditions for Fermi Type I and II resonances are satisfied to within a given tolerance (~200 cm^{-1}), affected near-zero terms are deleted from the relevant equations. The anharmonic energy levels for the resonant states are obtained by diagonalizing small resonance matrices with diagonal elements obtained from the equations for the anharmonic constants (with the resonant terms removed) and off-diagonal elements given by

$$\langle v_i + 1, v_j + 1, v_k | H | v_i, v_j, v_k + 1 \rangle = \phi_{ijk}\left(\frac{(v_i + 1)(v_j + 1)(v_k + 1)}{8}\right)^{\frac{1}{2}} \tag{2.54}$$

$$\langle v_i + 2, v_k | H | v_i, v_k + 1 \rangle = \phi_{iik}\left(\frac{(v_i + 1)(v_i + 2)(v_k + 1)}{32}\right)^{\frac{1}{2}} \tag{2.55}$$

$$\langle v_i + 2, v_k | H | v_i, v_k + 2 \rangle = K_{iikk}\left(\frac{(v_i + 1)(v_i + 2)(v_k + 1)(v_k + 2)}{16}\right)^{\frac{1}{2}} \tag{2.56}$$

where K_{iikk} is the Darling-Dennison constant [46, 47]. For the case of a general property, the above resonance matrices are not constructed but the resonance treatment for the perturbation theory expressions is carried out with removal of the resonant terms from the perturbation expression. In the perturbation theory expansion for a general property, the only terms unaffected by accidental vibrational resonance are the A terms in equations (2.39) and (2.40). Fortunately, these terms are also likely to yield the largest contribution to the vibrational correction so it is expected that vibrational resonance will not dramatically affect a property other than the energy. Presence of Coriolis resonance or Darling-Dennison resonance does not affect the perturbation theory expressions for a general property, but may need to be treated for the potential energy case.

Rotational corrections for a geometry-dependent property have been derived by Fowler for asymmetric [20], symmetric [19], and spherical top molecules [21, 48]. The rotational dependence of the property P on a rotational state $J\tau$ for the vibrational level υ of an asymmetric top is given by

$$\langle P\rangle_{\upsilon J\tau} - \langle P\rangle_{\upsilon 00} = \sum_{\alpha}\left(P^{\alpha} + \sum_{s} A_s^{\alpha}\left(\upsilon_s + \frac{1}{2}\right)\right)\left\langle J_{\alpha}^2\right\rangle_{J\tau} \tag{2.57}$$

where

$$P^{\alpha} = \sum_{s} C_s^{\alpha\alpha} P_s \tag{2.58}$$

$$A_s^{\alpha} = \frac{1}{2}\sum_{s'} C_{s'}^{\alpha\alpha} P_{sss'} \tag{2.59}$$

More complete formulae have been presented by Fowler [20] that include extra terms contributing to the A_s^{α} coefficient as well as a correction to the property from quartic centrifugal distortion. The equivalent formulae to equations (2.58) and (2.59) for symmetric top molecules are

$$P_J = \sum_{s} P_s C_s^{xx} \tag{2.60}$$

$$P_K = \sum_{s} P_s\left(C_s^{zz} - C_s^{xx}\right) \tag{2.61}$$

$$A_{sJ} = \frac{1}{2}\sum_{s'} P_{sss'} C_{s'}^{xx} \tag{2.62}$$

$$A_{sK} = \frac{1}{2}\sum_{s'} P_{sss'}\left(C_{s'}^{zz} - C_{s'}^{xx}\right) \tag{2.63}$$

$$A_{tJ} = \frac{1}{2}\sum_{s} P_{tts} C_{s}^{xx} \tag{2.64}$$

$$A_{tK} = \frac{1}{2}\sum_{s} P_{stt}\left(C_{s}^{zz} - C_{s}^{xx}\right) \tag{2.65}$$

In equations (2.60)-(2.65), $C_s^{\alpha\beta}$ is the dimensionless Watson C tensor [20], defined by

$$C_s^{\alpha\beta} = 4\pi\left(\frac{c}{h}\right)^{\frac{1}{2}} \frac{a_s^{\alpha\beta} B_\alpha B_\beta}{\omega_s^{\frac{3}{2}}} \tag{2.66}$$

where B_α are rotational constants and $a_s^{\alpha\beta}$ is the partial first derivative of the inertia tensor, $I_{\alpha\beta}$, with respect to the normal coordinates, Q_s, evaluated at the potential energy minimum. The above equations also assume that the highest order rotation axis of the symmetric top molecule coincides with the z axis. Linear molecules are treated as symmetric tops, with some additional constraints on angular momentum, and are therefore assumed to be aligned along the z axis with the degenerate modes rotated to lie in the xz and yz planes. For a linear molecule, the terms containing $\phi_{tt't''}$ vanish, with the coefficients P_K, A_{sK}, and A_{tK} set to zero. The G_{tt} and $G_{tt'}$ terms, which were originally purely vibrational, now contain rotational contributions due to the Sayvetz condition [10] and are given by the equations

$$G_{tt} = -\frac{P_{ttit}}{48} - \frac{1}{8}\sum_{s} P_{stt}\phi_{stt}\Omega_{ts}^{\#} - \frac{1}{2}\sum_{s} C_s^{xx}\left\{2P_s + \sum_{s'} P_{ss's'}\left(\upsilon_s + \tfrac{1}{2}\right) + \sum_{t'} P_{st't'}\left(\upsilon_{t'} + 1\right)\right\} \tag{2.67}$$

$$G_{tt'} = \sum_{s} P_{stt'}\phi_{stt'}\Omega_{stt'}^{\#} - \sum_{s} C_s^{xx}\left\{2P_s + \sum_{s'} P_{ss's'}\left(\upsilon_{s'} + \tfrac{1}{2}\right) + \sum_{t''} P_{st''t''}\left(\upsilon_{t''} + 1\right)\right\} \tag{2.68}$$

Vibrational energy levels of a linear polyatomic molecule may also be perturbed by vibrational l-type doubling if two or more degenerate modes are excited [13]. Therefore, for a geometry-dependent property, l-type doubling will also perturb the "property levels". Through examinination of the formulae for the energy case, the l-type doubling constant $R_{tt'}$ for a property may be deduced to be

$$R_{tt'} = \frac{\left(P_{t_a t_a t'_a t'_a} - P_{t_a t_a t'_b t'_b}\right)}{4} - \sum_s P_{stt'} \phi_{stt'} \Omega_{tt's} \tag{2.69}$$

Through working with the above equations for symmetric top molecules, a misprint has been discovered in [19] for the G_{tt} term as well as the existence of an extra fourth property derivative component $P_{tatat'bt'b}$ for the $B_{tt'}$ term that would make the equations consistent with the energy case [12]. It may be noted that through the use of dimensionless normal coordinates, all of the coefficients in the above equations have the units of the property of interest and do not involve any unnecessary units related to the nuclear displacements as would be the case for internal or normal coordinates. Symmetric top equations for a general property, in an arbitrary vibrational-rotational state, reduce to those of an asymmetric top if degenerate modes are deleted, and to the diatomic case for a single mode. Other formulations of a property in an arbitrary rotational-vibrational state for diatomic molecules have been forwarded by Buckingham *et al.* [22, 49, 50] and Schlier [51].

Explicit formulae for the property in an arbitrary vibration-rotational state for spherical top molecules have been derived by Fowler [21]. Some minor misprints have been discovered, associated with the quartic property derivatives contributing to the X_{tt} and G_{tt} property vibrational coefficients to make the spherical top equations for the property consistent with the energy expression given by Hodgkinson *et al.* [15]. In the expressions for these coefficients, it is believed that there should be a factor of 2 before the quartic $P^{(2)}_{tttt}$ property derivative where the subscript t labels a triply degenerate mode. Replacing general property derivatives, P, with force constants, ϕ, addition of Coriolis corrections [14, 15] and halving certain cubic terms for the X, G, T and S coefficients then allows the energy anharmonicity constants to be calculated from the corrected expressions for the property vibrational average.

2.3 Thermal averaging

Thermal averages of bulk properties may be calculated by methods outlined by Bishop [52] and Wong *et al.* [16]. The thermal average of a geometry-dependent property P at a temperature T may be given by

$$\langle P \rangle^T = \frac{1}{Z_{vib}} \sum_{\upsilon} \langle P \rangle_{\upsilon} \, e^{-E_{\upsilon}/kT} + \frac{1}{Z_{rot}} \sum_{J\tau} \langle P \rangle_{J\tau} \, e^{-E_{J\tau}/kT} \tag{2.70}$$

where Z_{vib}, E_υ, $<P>_\upsilon$ and Z_{rot}, $E_{J\tau}$, $<P>_{J\tau}$ are the respective vibrational and rotational partition functions, state energies and properties and vibrational and rotational motions are assumed to be independent. If a complete set of vibrational energies is available, then the above equation is conveniently used and is accurate, although it is likely to break down at high temperatures. Summations are over the energy states and so must be continued until the value of a particular sum changes by an acceptably small tolerance. A more approximate method devised by Toyama *et al.* [53] and extended by Jameson [25] ignores nuclear spin statistics, treats the rotational levels classically and assumes that all vibrational anharmonicity is neglected. Their expression for the thermal average of a property, P, at a temperature, T, is given by

$$\langle P \rangle^T = P_e + \langle P \rangle^T_{vib} + \langle P \rangle^T_{rot} \tag{2.71}$$

and

$$\langle P \rangle^T_{vib} = P_0 + \frac{1}{2}\sum_i g_i A_i \coth\left(\frac{hc\omega_i}{2kT}\right) + \frac{1}{4}\sum_{i \le j} g_i g_j B_{ij} \coth\left(\frac{hc\omega_i}{2kT}\right)\coth\left(\frac{hc\omega_j}{2kT}\right) \tag{2.72}$$

$$\langle P \rangle^T_{rot} = \frac{kT}{2hc}\sum_\alpha \frac{1}{B^e_\alpha}\left(P^\alpha + \frac{1}{2}\sum_i A^\alpha_i\right) \tag{2.73}$$

where g_i is the degeneracy of the ith vibrational mode of harmonic frequency ω_i, B^e_α are the rotational constants in cm^{-1}, P_0, A_i, B_{ij}, P^α and A^α_i are the vibrational and rotational coefficients from equations (2.34)-(2.37) and equations (2.58) and (2.59). The advantage of the approximate approach is that the thermal averages can be calculated using the known vibrational and rotational coefficients and no explicit summation over vibrational or rotational states is necessary. The main disadvantage is the loss of accuracy incurred at high temperatures from the approximations used. However, the majority of measurements of electrical properties are made at low temperatures (T < 500 K) so the loss of accuracy is not a serious concern for many applications. Due to the availability of accurate energy levels for acetylene [34], the sum-over-states expression (equation (2.70)) was utilised for computation of thermal averages for acetylene in Chapter 5. For the other investigations presented within this thesis, property thermal averages were computed via the approximate expression, given by equation (2.71).

2.4 Electrical properties of molecules

The energy of a charge distribution in a non-uniform static electric field is [54]

$$\begin{aligned} E = E_0 &- \mu_\alpha F_\alpha - \frac{1}{2}\alpha_{\alpha\beta} F_\alpha F_\beta - \frac{1}{6}\beta_{\alpha\beta\gamma} F_\alpha F_\beta F_\gamma - \frac{1}{24}\gamma_{\alpha\beta\gamma\delta} F_\alpha F_\beta F_\gamma F_\delta \\ &- \frac{1}{3}\Theta_{\alpha\beta} F_{\alpha\beta} - \frac{1}{3}A_{\gamma:\alpha\beta} F_\gamma F_{\alpha\beta} - \frac{1}{6}B_{\alpha\beta:\gamma\delta} F_\alpha F_\beta F_{\gamma\delta} \\ &- \frac{1}{6}C_{\alpha\beta:\gamma\delta} F_{\alpha\beta} F_{\gamma\delta} - \ldots \end{aligned} \tag{2.74}$$

Here E_0 is the field-free energy of the charge distribution, μ is the permanent electric dipole moment, α is the dipole polarizability, β and γ the first and second hyperpolarizabilities, A and B are the mixed dipole-quadrupole polarizability and hyperpolarizability, and C is the quadrupole polarizability. The quantities F_α and $F_{\alpha\beta}$ are the external electric field and electric field gradient respectively and the Greek subscripts denote summations over cartesian coordinates x, y and z. The electric dipole and quadrupole moments in the presence of the field are given by

$$\begin{aligned} \mu_\alpha = \mu_\alpha^0 &+ \alpha_{\alpha\beta} F_\beta + \frac{1}{2}\beta_{\alpha\beta\gamma} F_\beta F_\gamma + \frac{1}{6}\gamma_{\alpha\beta\gamma\delta} F_\beta F_\gamma F_\delta \\ &+ \frac{1}{3}A_{\alpha:\beta\gamma} F_{\beta\gamma} + \frac{1}{3}B_{\alpha\beta:\gamma\delta} F_\beta F_{\gamma\delta} + \ldots \end{aligned} \tag{2.75}$$

$$\Theta_{\alpha\beta} = \Theta_{\alpha\beta}^0 + A_{\gamma:\alpha\beta} F_\gamma + \frac{1}{2}B_{\gamma\delta:\alpha\beta} F_\gamma F_\delta + C_{\alpha\beta:\gamma\delta} F_{\gamma\delta} + \ldots \tag{2.76}$$

where the above equations define static response polarizabilities and hyperpolarizabilities in the presence of a static electric field. There are also dynamic polarizabilities and hyperpolarizabilities that are defined in terms of the response of the dipole and quadrupole moments to an oscillating electric field. Perturbation theory expressions for the evaluation of the static and dynamic properties are given by Buckingham [54]. In the present thesis, only the dipole moment, quadrupole moment and dipole polarizability tensor are studied. For the present purposes, the generic name, polarizability, is assumed to refer only to the dipole-polarizability and not the higher-order quantities. The quadrupole moment is also defined to be traceless. The number of independent components of the electrical property tensors is dictated by the symmetry of the molecule; these have been tabulated for various

point groups by Buckingham [54]. The dipole polarizability tensor may be decomposed into isotropic and anisotropic terms: the mean polarizability, α, and the polarizability anisotropy, $\Delta\alpha$, respectively defined by

$$\alpha = \frac{1}{3}Tr(\alpha_{\alpha\beta}) = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) = \frac{1}{3}\alpha_{\alpha\alpha} \tag{2.77}$$

$$\Delta\alpha = \left|\left\{\frac{1}{2}\left[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{xx} - \alpha_{zz})^2 + (\alpha_{yy} - \alpha_{zz})^2\right]\right\}^{\frac{1}{2}}\right| \tag{2.78}$$

where Tr is the trace (sum of diagonal elements) of the matrix. For molecules with a three-fold or higher-order principal axis of rotation, the perpendicular tensor elements are equal and therefore $\alpha_{xx} = \alpha_{yy}$ in the above expressions, leading to

$$\alpha = \frac{1}{3}(2\alpha_{xx} + \alpha_{zz}) \tag{2.79}$$

$$\Delta\alpha = (\alpha_{zz} - \alpha_{xx}) \tag{2.80}$$

where the parallel component of the polarizability tensor, α_{zz}, is directed along the z axis. An associated quantity, the Rayleigh depolarization ratio from light scattering experiments [55, 56], is related to the polarizability and polarizability anisotropy via the equation

$$\rho_0 = \left(\frac{3(\Delta\alpha)^2}{45\alpha^2 + 4(\Delta\alpha)^2}\right) \tag{2.81}$$

Particular care must be taken in calculating vibrational corrections for asymmetric top molecules because the vibrationally corrected $\Delta\alpha$ must be calculated from the full vibrationally corrected polarizability tensor. It is instructive to see why this is the case by using the general definition of the polarizability anisotropy for an asymmetric top molecule with the total vibrational state dependent polarizability tensor defined as

$$\left\langle \alpha_{\alpha\beta}^{total} \right\rangle_v = \alpha_{\alpha\beta}^{el} + \left\langle \alpha_{\alpha\beta}^{vib} \right\rangle_v \tag{2.82}$$

where $\alpha_{\alpha\beta}^{el}$ is the vibrationless electronic polarizability tensor and $\left\langle \alpha_{\alpha\beta}^{vib} \right\rangle_{\upsilon}$ is the vibrational correction to the polarizability for a particular vibrational state and may include the pure vibrational contribution for the same vibrational state, depending on the experiment and/or theoretical situation of interest. Substituting the above definition for the total polarizability into the equation for $\Delta\alpha$, the expression for the vibrational state dependent polarizability anisotropy is given by

$$\langle \Delta\alpha \rangle_{\upsilon} = \left[\left(\Delta\alpha^{el}\right)^2 + \left(\Delta\alpha^{vib}\right)^2 + \alpha_{\alpha\alpha}^{el}\left(2\alpha_{\alpha\alpha}^{vib} - \alpha_{\beta\beta}^{vib} - \alpha_{\gamma\gamma}^{vib}\right) \right]^{\frac{1}{2}} \tag{2.83}$$

It is clear from this discussion that the ZPVC to $\Delta\alpha$ for an asymmetric top molecule is only defined with respect to the equation

$$\text{ZPVC(Asymmetric top)} = \langle \Delta\alpha \rangle_{\upsilon=0} - \Delta\alpha^{el} \tag{2.84}$$

This equation is also valid for a symmetric top molecule, but in this case because $\langle \Delta\alpha \rangle_{\upsilon} = \Delta\alpha^{el} + \Delta\alpha^{vib}$,

$$\text{ZPVC(Symmetric top)} = \Delta\alpha^{vib} \tag{2.85}$$

2.5 Pure vibrational polarizabilities

For properties such as the polarizability, α, and hyperpolarizabilities, β, γ that represent responses of the electron distribution to a perturbing electric field, there are pure vibrational counterparts which arise from the distortion of the vibrational wavefunctions in the presence of the field [52, 57-59]. Several recent articles [57, 58, 60-64] present vibrational contributions to (hyper)polarizabilities, including applications of the finite field approach to the calculation of vibrational property derivatives [60, 64] and all include vibrational averaging, although not necessarily in a transparent manner. Martí and Bishop [59] have clarified the distinction between vibrational averaging and pure vibrational contributions, as well as the relationship between two methods commonly used for deriving vibrational (hyper)polarizabilities. The zero-point correction, α^{ZP}, and pure vibrational polarizability, α^{υ}, utilised by Martí and Bishop [59] are precisely the same as the ZPVC and α^{v}, respectively, as calculated in the present thesis. In this thesis, perturbation theory

expressions of Bishop and Kirtman [57, 58] are used to obtain the pure vibrational polarizability tensor, but the relevant equations have been expressed in a slightly different form to utilise dimensionless normal coordinates, q_i, rather than normal coordinates, Q_i. Bishop and Kirtman's formulae are also straightforwardly applied to other vibrational response properties such as the vibrational first-hyperpolarizability, β^{v}, vibrational second-hyperpolarizability, γ^{v}, and vibrational quadrupole polarizability, C^{v}, if dipole polarizability, quadrupole moment and hyperpolarizability derivatives are available.

The dipole moment, μ_α, is expanded in a Taylor series of the dimensionless normal coordinates

$$\mu_\alpha = \mu_\alpha^e + \sum_i \mu_\alpha^i q_i + \frac{1}{2}\sum_{i,j} \mu_\alpha^{ij} q_i q_j + \ldots \tag{2.86}$$

where the respective derivatives may be identified by comparing the above with equation (2.33). In their perturbation theory derivation, Bishop and Kirtman [57, 58] included all derivatives up to third order in the energy and second order in the dipole moment. Following the partitioning method of Bishop and Kirtman into terms involving orders of electrical and mechanical anharmonicity, the following expressions are derived

$$\left[\mu^2\right]^{0,0} = \sum_i \mu_\alpha^i \mu_\beta^i \frac{\omega_i}{\left(\omega_i^2 - \omega_\sigma^2\right)} \tag{2.87}$$

$$\left[\mu^2\right]^{2,0} = \frac{1}{2}\sum_{i,j} \mu_\alpha^{ij} \mu_\beta^{ij} \left[\frac{\omega_i}{\left(\omega_i + \omega_j\right)^2 - \omega_\sigma^2}\right] \tag{2.88}$$

$$\left[\mu^2\right]^{1,1} = -\frac{1}{2}\sum_{i,j,k} \frac{\omega_k}{\left(\omega_k^2 - \omega_\sigma^2\right)} \left\{ 2\phi_{ijk} \mu_\alpha^{ij} \mu_\beta^k \left[\frac{\omega_j}{\left(\omega_i + \omega_j\right)^2 - \omega_\sigma^2}\right] + \left(\frac{\phi_{iij}}{\omega_j}\right) \mu_\alpha^{jk} \mu_\beta^k \right\} \tag{2.89}$$

where ω_i are the harmonic vibrational frequencies and ω_σ is the optical frequency or the frequency of the induced dipole moment of interest. The pure vibrational polarizability tensor, $\alpha_{\alpha\beta}^{v}$, is then given by

$$\alpha^{v}_{\alpha\beta} = [\mu^2] = [\mu^2]^{0,0} + [\mu^2]^{2,0} + [\mu^2]^{1,1} \tag{2.90}$$

The square bracket notation used by Bishop and Kirtman, $[X]^{n,m}$, subdivides the vibrational contributions into orders of anharmonicity where n is the order of electrical anharmonicity and m is the order of mechanical anharmonicity.

Pure vibrational contributions to the polarizability and polarizability anisotropy arise in experiments where the measurements are based on the application of an external electric field that may be either oscillating ($\omega_\sigma > 0$) or static ($\omega_\sigma = 0$). Examples of such experiments are the field-induced Stark effect [65] and the Kerr effect [66] both of which may be generally used to obtain α and $\Delta\alpha$, and the dielectric permittivity [67] from which α can be obtained for non-dipolar molecules via the Clausius-Mossotti relation [68].

2.6 Property derivative transformations

Although dimensionless normal coordinates q represent a convenient system of coordinates for perturbation theory expressions, curvilinear internal coordinates $\mathcal{R}$ are more appropriate for use in isotopic substitution studies. These coordinates are geometrically defined and isotopically mass independent which implies that any property derivatives with respect to such coordinates may be transferred between isotopomers. Due to the curvilinear nature of these coordinates, as opposed to rectilinear normal coordinates [8], they should offer better convergence in a Taylor series expansion and provide a simpler description of intramolecular vibrational motion. Additionally, once the property derivatives in internal coordinates have been calculated for a given parent molecule, they may be used to study all of the isotopomers (or children) of the parent, thus saving the potentially expensive calculation of a set of property derivatives for each of the isotopomers. Curvilinear internal coordinates may be expressed in terms of the dimensionless normal coordinates as

$$\mathcal{R}_i = \sum_r L_i^r q_r + \frac{1}{2}\sum_{r,s} L_i^{rs} q_r q_s + \frac{1}{6}\sum_{r,s,t} L_i^{rst} q_r q_s q_t + \frac{1}{24}\sum_{r,s,t,u} L_i^{rstu} q_r q_s q_t q_u + \ldots \tag{2.91}$$

where the L_i^r, L_i^{rs}, L_i^{rst} and L_i^{rstu} are the respective first, second, third and fourth-order **L** tensor derivatives. Formulae for the **L** tensor elements up to third-order are presented in Hoy, Mills and Strey [8] for bond-stretching, linear and non-linear angle bending, out-of-plane bending and torsional coordinates. The definitions of the internal coordinates are also

provided in that work. Formulae for the bond-stretching and non-linear angle-bending fourth-order **L** tensor elements have been derived by Fowler and Raynes [24]. A geometry-dependent property may be expanded in a Taylor series of the curvilinear internal coordinates about the equilibrium geometry

$$P^{\mathcal{I}} = P_e^{\mathcal{I}} + \sum_i P_i^{\mathcal{I}} \mathcal{I}_i + \frac{1}{2}\sum_{i,j} P_{ij}^{\mathcal{I}} \mathcal{I}_i \mathcal{I}_j + \frac{1}{6}\sum_{i,j,k} P_{ijk}^{\mathcal{I}} \mathcal{I}_i \mathcal{I}_j \mathcal{I}_k + \frac{1}{24}\sum_{i,j,k,l} P_{ijkl}^{\mathcal{I}} \mathcal{I}_i \mathcal{I}_j \mathcal{I}_k \mathcal{I}_l + \ldots \tag{2.92}$$

which may be compared with equation (2.33) for the dimensionless normal coordinates. The transformation of curvilinear internal coordinate property derivatives into dimensionless normal coordinate property derivatives is represented by

$$P_r = \sum_i P_i^{\mathcal{I}} L_i^r \tag{2.93}$$

$$P_{rs} = \sum_i P_i^{\mathcal{I}} L_i^{rs} + \sum_{i,j} P_{ij}^{\mathcal{I}} L_i^r L_j^s \tag{2.94}$$

$$P_{rst} = \sum_i P_i^{\mathcal{I}} L_i^{rst} + \sum_{i,j} P_{ij}^{\mathcal{I}} \left(L_i^r L_j^{st} + L_i^s L_j^{tr} + L_i^t L_j^{rs} \right) + \sum_{i,j,k} P_{ijk}^{\mathcal{I}} L_i^r L_j^s L_k^t \tag{2.95}$$

$$\begin{aligned} P_{rstu} = & \sum_i P_i^{\mathcal{I}} L_i^{rstu} + \sum_{i,j} P_{ij}^{\mathcal{I}} \left(L_i^{rs} L_j^{tu} + L_i^{rt} L_j^{su} + L_i^{ru} L_j^{st} \right) \\ & + \sum_{i,j} P_{ij}^{\mathcal{I}} \left(L_i^r L_j^{stu} + L_i^s L_j^{tur} + L_i^t L_j^{urs} + L_i^u L_j^{rst} \right) \\ & + \sum_{i,j,k} P_{ijk}^{\mathcal{I}} \left(L_i^r L_j^s L_k^{tu} + L_i^r L_j^t L_k^{su} + L_i^r L_j^u L_k^{st} + L_i^s L_j^t L_k^{ru} + L_i^s L_j^u L_k^{rt} + L_i^t L_j^u L_k^{rs} \right) \\ & + \sum_{i,j,k,l} P_{ijkl}^{\mathcal{I}} L_i^r L_j^s L_k^t L_l^u \end{aligned} \tag{2.96}$$

where r, s, t and u are summation indices over the dimensionless normal coordinates with i, j, k and l representing summation indices over the curvilinear internal coordinates. The above set of equations may be formulated into two-, three- and four-index transformations for which there are efficient computer algorithms available [69].

If the property P in the above equations is the potential energy, then the first derivatives of the property (the energy gradient) vanish at a stationary point on the potential energy surface. The above equations are simplified for the energy case since only the **L** tensor up to third-order is required whereas for a general property with non-zero first derivatives, the fourth-order **L** tensor is required in equation (2.96). No **L** tensor formulae

for the fourth-order elements of non-linear angle bending, out-of-plane bending or torsional coordinates have yet been derived so at present the transformation of property derivatives for molecules with these internal coordinate types are limited to third-order. The above equations give the transformation from the internal coordinate $\mathcal{R}$ derivatives into dimensionless normal coordinate q derivatives. The inverse transformation of dimensionless normal coordinate derivatives into internal coordinate derivatives requires use of the $\mathbf{L}^{-1}$ matrix, otherwise known as the inverse of the first derivative **L** tensor. Following methods similar to those outlined by Maslen *et al.* [69], the $\mathbf{L}^{-1}$ matrix can be calculated and equation (2.93) may then be pre-multiplied by this matrix. Once the $P_i^{\mathcal{R}}$ have been constructed, equation (2.94) may be rearranged to give

$$P_{ij}^{\mathcal{R}} = \sum_{r,s} \left(L_i^r\right)^{-1} \left(L_j^s\right)^{-1} \left(P_{rs} - \sum_i P_i^{\mathcal{R}} L_i^{rs} \right) = \sum_{r,s} \left(L_i^r\right)^{-1} \left(L_j^s\right)^{-1} \left(P_{rs}^*\right) \tag{2.97}$$

Therefore the previous $(n-1)$th order of internal coordinate property derivatives determine the current nth order internal coordinate property derivatives. This applies to any order of the derivative transformation, so that once the **L** tensor has been constructed, only the $\mathbf{L}^{-1}$ matrix is additionally required. The **Y** tensor proposed by Green *et al.* [70] for the transformation from dimensionless normal coordinate derivatives, P, into internal coordinate derivatives, $P^{\mathcal{R}}$, is unnecessary and is likely to lead to extra computational cost for this transformation since the full **L** tensor is also required.

The above transformation equations have been implemented primarily for computation of the effects of isotopic substitution on electrical properties; the general method for obtaining isotope effects is discussed in the following section.

2.7 Isotope effects

An example of the general procedure for obtaining the property derivatives for isotopomers is displayed schematically as

$$P(q)\ \{\mathrm{H}\} \xrightarrow{L^*} P(\mathcal{R}) \xrightarrow{L} P(q)\ \{\mathrm{D}\}$$

where the property derivatives for the parent molecule are first transformed to the isotopically independent curvilinear internal coordinate system and then converted into the $P(q)$ property derivatives for the deuterated species or isotopomer of interest using a new **L** tensor for the specific isotopomer where the $\mathbf{L}^*$ tensor is used to denote an inverse transformation requiring use of the $\mathbf{L}^{-1}$ matrix. The $P(q)$ {D} derivatives for the energy and the property may then be used in the relevant equations to calculate the property vibrational corrections and pure vibrational polarizabilities for the isotopomer of interest. Special care must be taken in treating properties that are origin dependent; in these instances, the equilibrium properties after isotopic substitution must be referenced to the new centre of mass of the isotopomer. Although the symbols H and D have been used schematically, specific only to deuterium substitution of hydrogen, the above isotopic substitution may be carried out using any two isotopomers, for example the $^{12}CH_4$ and $^{13}CH_4$ species.

This general procedure has been utilised for calculation of the effects of deuterium substitution on the electrical properties for the second-row hydrides (Chapter 4), ethene (Chapter 7) and ethane (Chapter 8). For the study of acetylene in Chapter 5, a full property derivatives calculation was carried out on DCCD, thus bypassing the **L** tensor transformation.

References

[1] Born, M., and Oppenheimer, J. R., 1927, *Ann. Phys.*, **84**, 457.

[2] Levine, I. N., 1991, *Quantum Chemistry* (Prentice Hall, New Jersey).

[3] Hohenberg, P., and Kohn, W., 1964, *Phys. Rev. B*, **136**, 864.

[4] Møller, C., and Plesset, M. S., 1934, *Phys. Rev.*, **46**, 618.

[5] Bartlett, R. J., 1989, *J. phys Chem.*, **93**, 1697.

[6] Watson, J. K. G., 1968, *Molec. Phys.*, **15**, 479.

[7] Eckart, C., 1935, *Phys. Rev.*, **47**, 552.

[8] Hoy, A. R., Mills, I. M., and Strey, G., 1972, *Molec. Phys.*, **24**, 1265.

[9] Papousek, D., and Aliev, M. R., 1982, *Molecular Vibration-Rotational Spectra* (Elsevier).

[10] Nielsen, H. H., 1959, In *Handbuch der Physik*, Vol. Band XXXVII/I, edited by S. Flügge (Springer-Verlag), p. 209.

[11] Nielsen, H. H., 1951, *Rev. Mod. Phys.*, **23**, 90.

[12] Willetts, A., and Handy, N. C., 1995, *Chem. Phys. Lett.*, **235**, 286.

[13] Allen, W. D., Yamaguchi, Y., Csaszar, A. G., Clabo, D. A., Remington, R. B., and Schaefer, H. F., 1990, *Chem. Phys.*, **145**, 427.

[14] Hecht, K. T., 1960, *J. molec. Spec.*, **5**, 355.

[15] Hodgkinson, D. P., Heenan, R. K., Hoy, A. R., and Robiette, A. G., 1983, *Molec. Phys.*, **48**, 193.

[16] Wong, A. T., Bacskay, G. B., Hush, N. S., and Bogaard, M. P., 1991, *Molec. Phys.*, **74**, 1037.

[17] Willetts, A., Handy, N. C., Green, W. H., and Jayatilaka, D., 1990, *J. phys Chem.*, **94**, 5608.

[18] Riley, G., Raynes, W. T., and Fowler, P. W., 1979, *Molec. Phys.*, **38**, 877.

[19] Fowler, P. W., 1981, *Molec. Phys.*, **43**, 591.

[20] Fowler, P. W., 1982, *Molec. Phys.*, **46**, 913.

[21] Fowler, P. W., 1984, *Molec. Phys.*, **51**, 1423.

[22] Buckingham, A. D., and Urland, W., 1975, *Chem. Rev.*, **75**, 113.

[23] Fowler, P. W., 1983, *Molec. Phys.*, **48**, 153.

[24] Fowler, P. W., and Raynes, W. T., 1981, *Molec. Phys.*, **43**, 65.

[25] Jameson, C. J., 1977, *J. chem. Phys.*, **67**, 2814.

[26] Jameson, A. K., Schuett, K., Jameson, C. J., Cohen, S. M., and Parker, H., 1977, *J. chem. Phys.*, **67**, 2821.

[27] Bishop, D. M., 1993, *J. chem. Phys.*, **98**, 3179.

[28] Hush, N. S., and Reimers, J. R., 1995, *J. phys Chem.*, **99**, 15798.

[29] Buckingham, A. D., Fowler, P. W., and Galwas, P. A., 1987, *Chem. Phys.*, **112**, 1.

[30] Freedman, T. B., and Nafie, L. A., 1994, *Adv. chem. Phys.*, **85**, 207.

[31] Kawaguchi, K., and Tanaka, T., 1977, *J. molec. Spec.*, **68**, 125.

[32] Tanaka, K., Ito, H., Harada, K., and Tanaka, T., 1984, *J. chem. Phys.*, **80**, 5893.

[33] Tanaka, K., Ito, H., and Tanaka, T., 1987, *J. chem. Phys.*, **87**, 1557.

[34] Bramley, M. J., Carter, S., Handy, N. C., and Mills, I. M., 1993, *J. molec. Spec.*, **157**, 301.

[35] Schwenke, D. W., 1992, *Comput. Phys. Commun.*, **70**, 1.

[36] Dunn, K. M., Boggs, J. E., and Pulay, P., 1986, *J. chem. Phys.*, **85**, 5838.

[37] Whitehead, R. J., and Handy, N. C., 1975, *J. molec. Spec.*, **55**, 365.

[38] Whitehead, R. J., and Handy, N. C., 1976, *J. molec. Spec.*, **59**, 459.

[39] Cashion, J. K., 1963, *J. chem. Phys.*, **39**, 1872.

[40] Cooley, J. W., 1961, *Math. Computation*, **15**, 363.

[41] Dykstra, C. E., 1988, *Ab initio calculation of the structures and properties of molecules* (Elsevier).

[42] Dykstra, C. E., and Malik, D. J., 1987, *J. chem. Phys.*, **87**, 2806.

[43] Wilson, E. B., Decius, J. C., and Cross, P. C., 1955, *Molecular Vibrations. The theory of infrared and Raman vibrational spectra* (McGraw-Hill).

[44] Atkins, P. W., 1983, *Molecular Quantum Mechanics* (Oxford University Press).

[45] Alvarez-Collado, J. R., and Buenker, R. J., 1992, *J. Comp. Chem.*, **13**, 135.

[46] Mills, I. M., and Robiette, A. G., 1985, *Molec. Phys.*, **56**, 743.

[47] Amos, R. D., Handy, N. C., Green, W. H., Jayatilaka, D., Willetts, A., and Palmieri, P., 1991, *J. chem. Phys.*, **95**, 8323.

[48] Raynes, W. T., Fowler, P. W., Lazzeretti, P., Zanasi, R., and Grayson, M., 1988, *Molec. Phys.*, **64**, 143.

[49] Buckingham, A. D., 1962, *J. chem. Phys.*, **36**, 3096.

[50] Buckingham, A. D., and Cordle, J. E., 1974, *Molec. Phys.*, **28**, 1037.

[51] Schlier, C., 1961, *Fortschr. Phys.*, **9**, 455.

[52] Bishop, D. M., 1990, *Rev. Mod. Phys.*, **62**, 343.

[53] Toyama, M., Oka, T., and Morino, Y., 1964, *J. molec. Spec.*, **13**, 193.

[54] Buckingham, A. D., 1967, *Adv. chem. Phys.*, **12**, 107.

[55] Alms, G. R., Burnham, A. K., and Flygare, W. H., 1975, *J. chem. Phys.*, **63**, 3321.

[56] Bogaard, M. P., Buckingham, A. D., Pierens, R. K., and White, A. H., 1978, *J. Chem. Soc. Faraday Trans. I*, **74**, 3008.

[57] Bishop, D. M., and Kirtman, B., 1991, *J. chem. Phys.*, **95**, 2646.

[58] Bishop, D. M., and Kirtman, B., 1992, *J. chem. Phys.*, **97**, 5255.

[59] Martí, J., and Bishop, D. M., 1993, *J. chem. Phys.*, **99**, 3860.

[60] Martí, J., Andrés, J. L., Bertrán, J., and Duran, M., 1993, *Molec. Phys.*, **80**, 625.

[61] Kirtman, B., and Bishop, D. M., 1990, *Chem. Phys. Lett.*, **175**, 601.

[62] Bishop, D. M., and Cheung, L. M., 1979, *Phys. Rev. A*, **20**, 381.

[63] Bishop, D. M., Kirtman, B., Kurtz, H. A., and Rice, J. E., 1993, *J. chem. Phys.*, **98**, 8024.

[64] Cohen, M. J., Willetts, A., Amos, R. D., and Handy, N. C., 1994, *J. chem. Phys.*, **100**, 4467.

[65] Barnes, J. A., Gough, T. E., and Stoer, M., 1995, *Chem. Phys. Lett.*, **237**, 437.

[66] Buckingham, A. D., Bogaard, M. P., Dunmur, D. A., Hobbs, C. P., and Orr, B. J., 1970, *Trans. Faraday Soc.*, **66**, 1548.

[67] Bogaard, M. P., and Orr, B. J., 1975, In *International Review of Science, Physical Chemistry Series 2*, Vol. 2, edited by A. D. Buckingham (Butterworths), p. 149.

[68] Buckingham, A. D., 1972, In *MTP International Review of Science, Physical Chemistry Series 1*, Vol. 2, edited by A. D. Buckingham and G. Allen (Butterworths), p. 241.

[69] Maslen, P. E., Handy, N. C., Amos, R. D., and Jayatilaka, D., 1992, *J. chem. Phys.*, **97**, 4233.

[70] Green, W. H., Jayatilaka, D., Willetts, A., Amos, R. D., and Handy, N. C., 1990, *J. chem. Phys.*, **93**, 4965.