

The intermolecular potential energy surface of CO₂—Ar and its effect on collisional energy transfer

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1 Introduction

Classical molecular dynamics (MD) simulations [1, 2, 3, 4] are a useful tool for investigating many properties of molecular systems. To perform these simulations a complete potential energy surface (PES) is required. The PES completely describes the interactions of the constituent atoms in the molecular system, and unless one wants to perform an *ab initio* calculation at every step of the integration procedure this PES must be analytical.

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The PES is, unfortunately, not directly experimentally observable. One can infer information about the PES from experimental observables such as spectroscopic measurements, second virial coefficients and molecular-beam scattering data, but it is usually necessary to assume some functional form for the interaction and attempt to vary the parameters of the fit to reproduce the experimental results [5, 6, 7, 8, 9, 10].

Another route to the PES is via *ab initio* calculations, most commonly through electronic molecular orbital theory [11]. This is an expensive route as usually one would like to reasonably sample all degrees of freedom of the system. The computational cost of these calculations very quickly gets prohibitive for most *ab initio* approaches, even in small molecular systems. Not only do we face the cost of the *ab initio* calculations increasing typically at order N^3 or N^4 with the system size, but the number of single-point calculations required increases exponentially with the number of nuclear degrees of freedom of the system. Even when a set of data spanning the degrees of freedom of the system has been generated in this way some functional form must be fit to the data in order to be able to run MD simulations.

One issue which has not received much attention is the effect of the functional form used to fit the *ab initio* data and how good the fit needs to be for the MD simulation to produce meaningful results. Here we are addressing this question from the point of view of collisional energy transfer (CET) [12, 13]. A common approximation in CET studies, and one which lends itself to CET, is the separation of intermolecular and intramolecular degrees of freedom in the PES [12, 13]. CET is expected to be more sensitive to the intermolecular part of the PES than to the intramolecular part [12, 13]. This

behaviour has been indeed observed in this work, as the CET results do not change very much when the intramolecular potential is changed by excluding terms.

Since the aim of the present study is to examine the role of the intermolecular part of the PES in collisional energy transfer, we have chosen a simple test system, the collisional activation/deactivation of highly rovibrationally excited CO₂ molecule by a thermal Ar atom. This was motivated by the existence of a wide range of experimentally derived intermolecular potentials [5, 6, 7, 8, 9, 10] as discussed in section 2. Some previous experimental [14] and computational [6, 15, 16, 17] studies have been performed but they focussed largely on the high energy collisions of Ar with thermal CO₂ [6, 15, 16] or on the effect of anharmonicity and resonances [17] and hence are not closely relevant to the aims of the present study. It would be a natural progression of the present study to include similar systems, such as the collision of thermal noble gas atoms with highly excited molecules of SO₂ [12] or CS₂ [13], in further shape work, particularly because of the existence of extensive experimental data on CET and the lack of direct experimental or *ab initio* information on the shape of the intermolecular potential.

In section 2 we briefly describe the existing intermolecular potential surfaces and our new potential surface calculations. The fitting of various intermolecular pair potentials to the potential surface data is detailed in section 3. In section 4 the sensitivity of the CET to the various fitting approaches is reported and the results are discussed in section 5.

2 The potential energy surface and *Ab initio* calculations

Several intermolecular potential surfaces of the CO₂—Ar system have been proposed in the literature. The first serious attempts to account for the experimentally observed properties were made by Pack and co-workers in the mid-1970s [5, 6]. The work of Hough and Howard [8] and Bohac *et al.* [18] later produced quite a large number of broadly similar potentials. Hutson and co-workers recently produced their own versions of the potentials after concluding that none of the previous potentials were satisfactory [9, 10]. All of these potentials assumed some functional form for the interaction which was then least-squares fitted to the experimental data. In some cases the functional form of the interaction was based on theoretical or previously calculated data.

These potentials as they stand are unsuitable for performing classical MD simulations, as they include no motions of the CO₂ fragment. While it is possible to invent schemes that add CO₂ motion dependence, we have taken a different route to generate our full PES, though it could be considered to have similarities with the methods used for the most recent experimentally derived potential [10].

We have assumed complete separation of the PES into intramolecular and intermolecular parts, as is common in collisional energy transfer studies [12, 13]. For the internal motions of the CO₂ fragment we have used the potential used previously for CET studies by Suzukawa *et al.* [15]. This potential

comprises a sum of one Morse function for each C—O bond, a quadratic bending term and a quadratic bond coupling term. For the intermolecular part of the PES we have used a sum of three pair-wise additive functions, again a common practice in CET studies [12, 13]. The functional forms used are standard atom-centred radial potential functions [19], such as the Lennard-Jones n -6, Buckingham exp- α :6 and Morse functions.

The parameters for the various radial functions were obtained by fitting to a set of *ab initio* data. Our assumptions about the interaction meant that we could freeze the CO₂ fragment in the linear configuration with a C—O bond length of 1.16 Å. Freezing the CO₂ fragment reduces the number of scanned degrees of freedom in the system from six to two.

Two approaches have been taken to generating the *ab initio* surface in this work. On one hand we have used the GAUSSIAN 94 suite of programs [20] to generate samplings of the PES within the Møller-Plesset perturbation theory framework up to fourth order. The second approach to generating the PES sample points was to use density functional theory (DFT), implemented in the Amsterdam Density Functional (ADF) package [21]. Both approaches used the supermolecule method [22] of generating the interaction energy profile.

The main PES data used was generated by the GAUSSIAN package and is shown in figure¹. This *ab initio* surface was calculated at the MP4/6-311+G(2d) level of theory. The 6-311+G(2d) basis is relatively large, with 27 Gaussian basis functions centred on each atom. The DFT surface was

¹Contour plot of MP4 surface

calculated using the ADF package with the Vosko, Wilk and Nusair Local Density Approximation (VWN LDA) and Perdew-Wang 91 Generalised Gradient Approximation corrected functional. The basis set used was an ADF type V basis, which is a triple-zeta set of slater type orbitals with two polarisation functions per atom. The ADF and Gaussian basis sets used are of similar quality. A PES from a lower level MP2/6-311+G(2d) calculation was also used. These surfaces are qualitatively similar to the experimentally derived potentials [10].

An interesting point to note is the presence in all three *ab initio* surfaces of a secondary minimum in the potential. The MP n surfaces have a barrier between the potential in the linear geometry and the global minima of around 15 cm^{-1} . The DFT/PW91 potential has a barrier that is lower by a factor of three and located much closer to the T-shaped geometry. The existence of this barrier forming secondary minima is hotly contested. Some previous calculations have shown the secondary minima to exist [23, 24], while another recent *ab initio* study using a high level perturbation method has not found evidence of a secondary minima [25]. A second minimum is present in only three of the experimentally derived potentials mentioned above [5, 6, 8, 18, 9, 10]. The experimental data is considered insensitive to this part of the potential [10].

The interaction energies calculated were converged very well with basis set. The variation in the well region of the potential with the basis sets looked at here is a factor of four larger for the MP4 calculations than for the DFT calculation. This difference in variation is despite the similarity of the smallest basis sets used, which in each case were double zeta basis sets.

The conventional *ab initio* results [20] show interesting convergence properties with the level of theory used. The MP2 and MP4 energies are extremely similar. The MP3 interaction on the other hand produces a significantly shallower well. As expected the single determinant Hartree-Fock interaction did not possess an attractive well.

The DFT calculations [21] do not have this convergence with method. Five functionals were tested, all based on the VWN LDA with differing gradient corrections. The Becke-Perdew, B-LYP, van Leeuwen-Baerends and Perdew-Wang 91 gradient corrections were trialed in calculations on the well region of the PES. While the PW91 corrected functional produces intermolecular potentials which agree remarkably well with the experimental structure of the CO₂—Ar van der Waals complex and the potentials calculated using the GAUSSIAN package, the VWN LDA functional alone produces a well which is far too deep and located too close to the CO₂ fragment. No other functionals tested lead to the calculation of a bound state in the T-shaped geometry, *ie* the potentials had no well. This deficiency in the treatment of the well region is a consequence of the poor representation of the dispersion energy in current DFT functionals [19].

The depth of the CO₂—Ar intermolecular potential surface (and the corresponding C—Ar separation) for T-shaped and linear geometries is given in Table 1 for the *ab initio* and DFT/PW91 calculations and compared with recent experimental fits [10] and recent *ab initio* calculations [25]. The potential well is 157 cm⁻¹ deep at the potential minimum for the MP2 and MP4 surfaces (corresponding to the T-shaped complex geometry), and 177 cm⁻¹ deep for the DFT/PW91 surface. The MP2 and MP4 surfaces vary in the

Table 1: Depth (cm^{-1}) of intermolecular potential surface (and C—Ar separation (\AA)) for T-shaped and linear geometries of $\text{CO}_2\text{—Ar}$

Data Source	T-shaped	Linear
this work [26]		
MP2/6-311+G(2d)	157 (3.541)	128
MP4/6-311+G(2d)	157 (3.547)	135
ADF-DFT/PW91	177 (3.721)	137
Marshall <i>et al.</i> [25]		
MP4/Sdf(b-ext)	210 (3.456)	117 (4.763)
fitted	210 (3.475)	113 (4.708)
Hutson <i>et al.</i> [10]		
single repulsion model	204.16 (3.416)	126.30 (4.572)
split repulsion model	202.57 (3.417)	114.99 (4.589)

depth of the well in the linear geometry, being 128 cm^{-1} and 135 cm^{-1} respectively. The corresponding DFT/PW91 surface depth is 137 cm^{-1} . The well depths in the T-shaped geometry for the current MP4 calculations are too low (by 25%) when compared to the recent MP4 calculations of Marshall *et al.* [25]. They used an extended basis set supplied with bond functions and yielded well depths consistent with the recent experimentally derived surfaces of Hutson *et al.* [10].

The *ab initio* potentials used are summarised in figure². This shows slices through the potential surfaces at various angles, centred on the carbon atom of the CO_2 molecule. Also shown on this plot are slices through a potential generated as a pair-wise sum Lennard-Jones 12-6 terms with the parameters taken from the interactions between the next highest noble gas atoms—in this case neon and argon. This type of potential is often used for CET studies [12, 13] and results from this potential is also included in most of the analysis below.

3 Fit of pair potentials to intermolecular surface

As already stated, discrete samplings of the PES are not sufficient for running classical trajectory simulations [1, 2, 3, 4]. To then use our potentials for CET studies we have fit a variety of pair-wise additive functional forms to the *ab initio* data. The fit was performed by an iterative non-linear weighted least-

²Plot of MP2, MP4, ADF and Scoles

squares procedure. The χ^2 statistic [27] was used as the weighed residual sum of squares estimator, and the global minimum of the χ^2 surface was searched out as a function of the pair potential parameters using a conjugate gradient search method [28, 29].

The initial fits to the data included all the data up to a potential of 0.1 hartree, or 30000 K. In this case the points above about 0.01 hartree caused some of the fitted functions to reproduce the well region of the potential badly. This was despite the relatively low number of data points (less than 20% of the total number) and their low χ^2 weighting due to their high values.

To better reproduce the well region of the potential the data was re-fitted including only data below 0.01 hartree (3000 K). This is the important region of the PES for CET studies in a thermally distributed bath. The quality of the fit in the well region of the previously badly behaved potentials was generally greatly improved by this data set restriction, implying that these particular functional forms do not adequately represent the shape of the potential over a large energy range.

An important point to note with these potential fits is the variation with angle in the nature of the error in the well region. Take the potential constructed from Morse functions as an example, figure³. In the linear and T-shaped configurations (the rightmost and leftmost curves) the depth of the potential well and the curvature at the radial minimum are underestimated. However at 30 degrees from the linear approach the potential is reproduced well, while at 60 degrees from the linear approach the well depth is overesti-

³Plot of MP4 and Morse slices

mated. While it is possible that these effects are a sign of an incomplete fit, this is considered unlikely as this χ^2 minimum was approached from several different directions in the parameter space of the fit. It is far more likely that this is a demonstration of the inadequacy of approximating the true form of the PES by a sum of atom-centred Morse functions. All of the constructed pairwise potentials displayed this inadequacy to some extent.

4 Molecular dynamics calculations

For each potential fit a series of MD simulations was performed. In each batch of simulations the CO₂ fragment was set up in an initial state selected from the microcanonical ensemble using the efficient microcanonical sampling (EMS) procedure [30, 31]. The argon atom for each trajectory was set up with an initial velocity selected from a thermal distribution and an impact parameter selected from a uniform distribution with an upper limit of $b_{\max} = 15\text{\AA}$. The uniform distribution was used for the impact parameter b rather than the statistically correct distribution density, which is proportional to b , to more efficiently sample trajectories with a low impact parameter. These low impact parameter trajectories are more important for CET than the higher impact parameter ‘fly-bys’ [12].

The trajectories were integrated using a vectorised Velocity-Verlet integrator [4] until all (or all but a few) of the argon atoms in the batch of trajectories were more than 15 Å from the centre of mass of the CO₂ fragment. This was up to 61 ps of simulation time for some of the systems. We have demonstrated that our average energy transfer moments are converged

with increasing maximum impact parameter and decreasing integration step size.

The main quantities used to study the energy transfer as a function of initial internal energy E and bath temperature T were the average energy transfer per collision and the average squared energy transfer:

$$\langle \Delta E \rangle = \sum_{i=1}^n (E'_i - E) b_i / \sum_{i=1}^n b_i$$

$$\langle \Delta E^2 \rangle = \sum_{i=1}^n (E'_i - E)^2 b_i / \sum_{i=1}^n b_i.$$

The weighting by impact parameter in these expressions is to correct for the uniform impact parameter sampling. Whenever errors are quoted in this paper, we are referring to the standard error of the data set. This is given by

$$\text{SE} = \left[\left(\langle \Delta E^2 \rangle - \langle \Delta E \rangle^2 \right) / (n - 1) \right]^{1/2}.$$

The initial internal energy of the CO₂ fragment was set at five different values from 5 kcal/mol to 100 kcal/mol and the argon bath was sampled at four temperatures from 300 K to 1800 K. This gives a total of 20 batches of 10000 trajectories for each potential surface.

From the trajectory simulations one can generate a slice through the energy transfer kernel, $P(E'|E)$ [12]. A typical plot of this quantity is shown in figure⁴ for the noble gas Lennard-Jones PES. The features of this $P(E'|E)$ are common for relatively highly vibrationally excited molecules being relaxed toward thermal equilibrium with a bath gas. The $P(E'|E)$ plots of all

⁴Scoles P(E',E)

the potentials investigated are similar, with details such as the length and strength of the high energy transfer tail differing between models.

We have found that the energy transfer moments are very sensitive to the fit of the intermolecular potential. In the initial fits to the MP4 data the χ^2 value for the fits were generally in the range 0.08 to 0.008 for the 357 points fitted. The trajectory simulations on these potentials yielded some average energy transfer results that varied over almost an order of magnitude, as demonstrated in figure⁵. The variation between the results for each potential seems to increase with increasing initial internal energy of the CO₂ fragment, making those shown in the above figure at an initial internal energy of 100 kcal/mol one of the worst cases. Despite the differences, the bath temperature and initial internal energy dependence of these average energy transfer results were roughly the same for all the fitted potentials.

When the pair potentials were re-fitted to the *ab initio* data excluding data points with energies above 0.01 hartree, the energy transfer results changed most dramatically for those potentials which had previously been the worst at reproducing the well region of the *ab initio* data. The initial fit of the Morse functional form to the *ab initio* data produced a potential with a well around five times too shallow. When the Morse functions were re-fit to the *ab initio* data to better reproduce the potential well, the effect on the energy transfer was most pronounced at low temperatures, as one would expect. This is demonstrated in figure⁶. These different potentials had χ^2

⁵DRI, Buck, LJv2(bad), Morse dE.100.cor

⁶Morse old and new, 15 and 75

estimators of 0.06 and 0.003 respectively. Simply deleting the data above 0.01 hartree decreased the χ^2 estimator on the existing surfaces by a factor of around two.

A different effect is observed in the second moment, shown in figure⁷. The moments generated from the original, nearly well-less potential lie well within one standard error of the results from the re-fitted, more accurate potential for the higher bath temperatures looked at. However, there appears to be a definite systematic increase in the second moment arising from the re-fitted potential. This can be at least partially explained by the existence of the well inducing small energy transfers for argon trajectories skimming past the CO₂ molecule through the well region. These small energy transfers would widen the peak in the $P(E'|E)$ distribution around the initial energy, which is reflected in the increase in the second energy transfer moment. This argument is supported by the observation that when the first energy transfer moment is plotted as a function of maximum impact parameter (by progressively discarding trajectories with an impact parameter over the target b_{\max} in the analysis) the energy transfer moment converges at a b_{\max} 1–2 Å lower for the nearly well-less potential than for the potential with a reasonable potential well.

Once the potential forms have been fit in such a way as to specifically reproduce the region of the potential with energies around the typical translational energies of the bath atoms, the energy transfer results are far less variable with potential form. Most of the calculated average energy transfer

⁷Morse old and new, 15 and 75 dE2

results for the well-fit potentials lie within two standard errors of each other, as shown in figure⁸. The agreement here of the noble gas derived Lennard-Jones potential with the other energy transfer results is surprising, given the stark difference between this potential and the others. The second energy transfer moments also agree quite well in this case.

5 Discussion and conclusions

In the system we have studied here the pair potential approximation appears to be at least consistent. The convergence of the energy transfer moments when the different pairwise functional forms are fitted well to the important regions of the potential is evidence for this. It also appears that there are other errors, such as sampling errors and integration errors which can swamp any differences between the intermolecular potentials calculated using MP2/MP4 theory or DFT.

Contrary to expectations, the energy transfer moments calculated from the DFT/PW91 potential (see figure⁹) are in excellent agreement with the results of calculations on intermolecular potentials derived from the more computationally demanding and firmly based *ab initio* methods. However, as mentioned previously, it is clear that DFT does not give reliable results for properties such as intermolecular well depths (e.g. see Table 1) due to the poor handling of the dispersion energy in current functionals [19]. The consensus view is that DFT is of little practical use for the calculation of in-

⁸good morse, lj, MP2, ADF and Scoles dE.30.cor

⁹good morse, lj, MP2, ADF and Scoles dE.30.cor

termolecular potentials [32]. However, in further studies [26], we have noted that, at typical temperatures ($T > 300$ K) the repulsive wall of the intermolecular potential generally plays a much larger role in the efficiency of CET than the well. Initial trends shown in the present and further calculations [26] indicate that DFT methods may be suitable for approximate but inexpensive estimation of the efficiency of CET.

The energy transfer results are, however, sensitive to the quality of the fit of the functional forms to the *ab initio* data. With this in mind, the success of the noble gas-based Lennard-Jones interactions is remarkable given that this potential surface is so markedly different from the other potentials.

The lower temperature energy transfer results are sensitive to the potential well region, as expected. The data has not been analysed for the dependence on the angle- and time-averaged steepness of the repulsive wall, or the curvature of the wall. Angle dependent effects have not been identified.

In future, we plan to analyse the energy transfer results further with regard to specific features of the potential energy surface. For example, further calculations [26] have revealed a strong correlation of energy transfer with the steepness of the repulsive wall. We also plan to further investigate the pair-wise potential approximation and determine whether the experimentally derived potentials can be suitably expanded in terms of computationally inexpensive radially symmetric potentials.

6 Computational resources

The calculations reported on here were carried out on a number of machines, ranging from an RS-6000 workstation to the SGI Power Challenge and Fujitsu VPP300 supercomputers housed in the ANU Supercomputer Facility (ANUSF) (<http://anusf.anu.edu.au>). Thanks goes to ANUSF for generous allocations of time to run these calculations on these supercomputers.

References

- [1] D. L. Bunker, *Methods Comput. Phys.* 10 (1971) 287.
- [2] R. N. Porter and L. M. Raff, in: *Dynamics of molecular collisions*, vol. B, ed. W. H. Miller (Plenum, New York, 1976) p. 1.
- [3] L. M. Raff and D. L. Thompson, in: *Theory of chemical reaction dynamics*, vol. III, ed. M. Baer (CRC Press, Boca Raton, 1985) p. 1.
- [4] M. P. Allen and D. J. Tildesley, *Computer simulation of liquids* (Clarendon Press, Oxford, 1987).
- [5] G. A. Parker, R. L. Snow and R. T. Pack, *J. Chem. Phys.* 64 (1976) 1668.
- [6] R. K. Preston and R. T. Pack, *J. Chem. Phys.* 66 (1977) 2480.
- [7] A. M. Hough and B. J. Howard, *J. Chem. Soc., Faraday Trans. 2* 83 (1987) 173.

- [8] A. M. Hough and B. J. Howard, *J. Chem. Soc., Faraday Trans. 2* 83 (1987) 191.
- [9] C. F. Roche, A. Ernesti, J. M. Hutson and A. S. Dickinson, *J. Chem. Phys.* 104 (1996) 2156.
- [10] J. M. Hutson, A. Ernesti, M. M. Law, C. F. Roche and R. J. Wheatley, *J. Chem. Phys.* 105 (1996) 9130.
- [11] W. J. Hehre, L. Radom, P. v.R. Schleyer and J. A. Pople, *Ab initio molecular orbital theory* (John Wiley and Sons, New York, 1986).
- [12] S. Nordholm and H. W. Schranz, in: *Chemical kinetics and dynamics*, vol. 2A, ed. J. R. Barker (JAI, Connecticut, 1995) p. 245.
- [13] G. Lendvay and G. C. Schatz, in: *Chemical kinetics and dynamics*, vol. 2B, ed. J. R. Barker (JAI, Connecticut, 1995) p. 481.
- [14] D. J. Krajnovich, C. S. Parmenter and D. L. Catlett, Jr., *Chem. Rev.* 87 (1987) 237.
- [15] H. H. Suzukawa, Jr., M. Wolfsberg and D. L. Thompson, *J. Chem. Phys.* 68 (1978) 455.
- [16] G. D. Billing, *Chem. Phys.* 91 (1984) 327.
- [17] B. G. Sumpter, D. L. Thompson and D. W. Noid, *J. Chem. Phys.* 87 (1987) 1012.
- [18] E. J. Bohac, M. D. Marshall and R. E. Miller, *J. Chem. Phys.* 97 (1992) 4890.

- [19] A. J. Stone, *The theory of intermolecular forces* (Clarendon Press, Oxford, 1996).
- [20] M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez and J. A. Pople, *Gaussian 94* (Gaussian, Inc., Pittsburgh, PA, 1995). Revisions D and E.
- [21] ADF 2.3.0 (Theoretical Chemistry, Vrije Universiteit, Amsterdam, 1997).
- [22] R. Moszynski, T. G. A. Heijmen and B. Jeziorski, *Molec. Phys.* 88 (1996) 741.
- [23] R. G. A. Bone, *J. Phys. Chem.* 98 (1994) 3126.
- [24] R. G. A. Bone and R. F. W. Bader, *J. Phys. Chem.* 100 (1996) 10892.
- [25] P. J. Marshall, M. M. Szczyński, J. Sadlej, G. Chałasiński, M. A. ter Horst and C. J. Jameson, *J. Chem. Phys.* 104 (1996) 6569.
- [26] T. J. Frankcombe. Carbon dioxide in argon: computational studies of the intermolecular potential energy surface and collisional energy trans-

fer. Honours thesis, Research School of Chemistry and Department of Chemistry, ANU, Canberra, Australia, 1997.

- [27] M. J. Moroney, *Facts from figures*, second ed. (Penguin, London, 1990).
- [28] H. Anton, *Elementary linear algebra*, Sixth ed. (John Wiley & Sons, Singapore, 1991).
- [29] D. R. Kincaid and E. W. Cheney, *Numerical analysis* (Brooks/Cole Publishing, Pacific Grove, California, 1990).
- [30] H. W. Schranz, S. Nordholm and G. Nyman, *J. Chem. Phys.* 94 (1991) 1487.
- [31] E. S. Severin, B. C. Freasier, N. D. Hamer, D. L. Jolly and S. Nordholm, *Chem. Phys. Lett.* 57 (1978) 117.
- [32] N. C. Handy, in: *New challenges in computational quantum chemistry*, ed. P.J.C. Aerts R. Broer and P.S. Bagus (University of Groningen, Groningen, 1994) p. 59.