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On the use of pseudostates to calculate molecular polarizabilities

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Abstract

The polarizability of a molecule is an intrinsic property which is important for a large variety of problems. However, determining reliable values for these polarizabilities is not straightforward: for instance the standard sum over states formulation of the problem does not converge because of the need to include not only many excited states but also to allow for contributions from the continuum. Here a formulation of this technique is given which uses pseudostates to allow for physical and continuum states otherwise omitted from the expansion. The pseudostates are represented by even-tempered expansions of Gaussian-type orbitals at the molecular centre-of-mass. The method is tested for LiH, Li_2, water and CO molecules. For LiH and CO, calculations for the polarizability of low-lying excited states are presented including that for the A $^3\Pi$ state of CO, whose polarizability appears not to have been previously determined. It is suggested that the use of pseudostates provides a straightforward method of calculating static polarizabilities of molecules in both ground and excited electronic states. The extension of the method to the calculation of dynamic polarizabilities is discussed.

1. Introduction

The polarizability of a molecule is important for a variety of applications including laser studies and Raman spectroscopy, long-range potentials, the determination of dielectric constants, refractive indices and van der Waals coefficients. For example, the polarizability is part of the Langevin expression used to estimate the rate constant for ion–molecule reactions (Baer and Powis 1994). However, the determination of reliable molecular polarizabilities is not straightforward (Bonin and Kadar-Kallen 1994, Hohm 2000), particularly for open shell species and molecules in electronically excited states.

There are several methods available for the calculation of molecular polarizabilities (Bonin and Kadar-Kallen 1994, Kobus 2007). Here we concentrate on the sum-over-states (SOS) method which is derived from the second-order perturbation theory (Ditchfield *et al* 1970). In this method the components of the polarizability tensor can be expressed as

$$\alpha_{rs} = 2\sum_{n>0} \frac{\langle 0|\mu_r|n\rangle \langle n|\mu_s|0\rangle}{E_n - E_0}, \qquad (1)$$

where r and s represent the Cartesian components x, y and z. Here E_n and $|n\rangle$ represent the electronic energy and associated electronic wavefunction for the nth electronic state of the system, the state for which polarizability is being calculated in labelled $|0\rangle$, but does not have to be the ground state. Although the sum in equation (1) in principle runs over all states of the system, the rules governing dipole operator μ mean that only states with the same spin symmetry as $|0\rangle$ need to be considered and, for molecules with spatial symmetry, other symmetry constraints also apply. However, within the relevant space–spin symmetries the sum does run over *all* states, including those in the continuum. As illustrated by the example calculations presented below, for most cases the sum requires the consideration of many states, as well as the continuum, to achieve convergence. The requirement to consider a potentially infinite number of states clearly puts a serious constraint of the application of the SOS formulation for calculating polarizabilities.

Allison *et al* (1972) proposed an R-matrix theory of atomic polarizabilities based on the use of many states in the SOS formalism. Over time Allison *et al*'s method evolved into the R-matrix with pseudostates (RMPS) method (Bartschat and Burke 1987, Bartschat *et al* 1996). The RMPS is primarily aimed at the extension of electron–atom collision calculations to intermediate energies and, in particular, the explicit consideration of electron impact ionization. However, this method also allows for a reliable treatment of polarization effects in the collision, for which a realistic representation of the polarizability of the atomic target is important.

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More recently Gorfinkiel and Tennyson (2004, 2005) adapted the RMPS method to molecular problems; their procedure has a number of technical differences to the atomic RMPS method of Bartschat and co-workers, several of which are discussed below. Gorfinkiel and Tennyson observed that their method gave a significantly improved representation of the target polarizability compared to other electron–molecule scattering procedures; this property has been exploited in subsequent applications of the molecular RMPS procedure (Halmova and Tennyson 2008, Halmova *et al* 2008, Tarana and Tennyson 2008). Here we present a series of calculations designed to test the use of a molecular RMPS method for calculating molecular polarizabilities; both ground and excited target states are considered. In this initial study we focus on molecules whose polarizabilities are generally well known, at least for the electronic ground state. The molecules for which we present calculations are LiH, a few electron benchmark system for which ultrahigh accuracy calculations are available, Li_2, chosen because of its exceptionally large polarizabilty, CO and water.

2. Method

The basic idea of the RMPS method is the use of an extra basis set whose role is to represent all states not represented by the initial, standard target basis set. In an *R*-matrix procedure, it is only necessary to represent these states within the finite region of coordinate space represented by the inner region, which is given by a sphere centred on the target centre-of-mass and chosen to enclose the charge density of the target state(s) of interest. One effect of this sphere is that the continuum in the inner region is discretized. Here we do not work explicitly with an *R*-matrix procedure or an inner region, but the demands on the extra basis set are similar since only states whose transition dipole matrix $\langle 0|\mu|n\rangle$ is non-zero will contribute to the SOS summation. This will only be true for states which are located in the same region of coordinate space as the target state of interest which is denoted $|0\rangle$.

The molecular RMPS procedure of Gorfinkiel and Tennyson (2004, 2005) works with Gaussian type orbitals (GTOs). It augments the standard, atom-centred GTO, used to create the target molecular orbitals (MOs) and hence represents its wavefunction, with another set of GTOs located at the molecular centre-of-mass. For these GTOs an even-tempered basis (Schmidt and Ruedenberg 1979) is employed in which ζ, the exponents of the GTOs, can be written as

$$\zeta_i = \zeta_0\beta^{(i-1)}, \qquad i = 1, \ldots, L. \qquad (2)$$

By choosing different values of the parameters ζ_0 and β, different basis sets can be systematically generated. In principle this representation can yield a complete set (Wilson 1980).

Use of an extra set of basis functions can lead to problems with linear dependence. Numerical experiments (Gorfinkiel and Tennyson 2004, 2005) show that stable orbital sets can be obtained by Schmidt orthogonalizing the pseudo-orbitals (POs) to the target MOs and performing a symmetric orthogonalization within the POs. Orthogonalized POs which have eigenvalues of the overlap matrix that are lower than some deletion threshold, δ, are then removed from the basis. The new set of orbitals, MOs plus POs, are used as the basis for a configuration interaction (CI) calculation. In principle, for an *N*-electron system, these configurations can be written as

$$(\mathrm{MOs})^N$$
$$(\mathrm{MOs})^{N-1}\ (\mathrm{POs})^1.$$

In practice, it is only possible to perform the full CI calculation implied by the first set of configurations for systems with very few electrons. Similarly, it is easy for the number of configurations generated by the second set to also become very large. Practical procedures for selecting suitable configuration sets will be given in the illustrative calculations below.

Finally, we note that augmenting the target MOs with a set of diffuse functions allows not only the representation of high-lying excited states and (quasi-)continuum, it also adds considerably to the flexibility available to the ground state wavefunction. The addition of these functions, which help converge polarization effects in the ground state, means that good results can be obtained with relatively small, standard target basis sets. All calculations reported below used s, p and d pseudo-orbital basis functions. Tests showed that inclusion of higher angular momentum functions made essentially no difference to the calculated polarizabilities. However, it is to be anticipated that these functions will become important for calculations on heavier molecules which have d electrons. Indeed high angular momentum pseudostates have been proved important in other contexts (Zhang *et al* 2010).

3. Calculations

Although the method proposed here should be reasonably straightforward to implement in a standard quantum chemistry code, the calculations were all actually performed using the UK Molecular *R*-matrix codes (Morgan *et al* 1998) since the procedure was already available. These codes are heavily optimized for electron–molecule scattering problems (Tennyson 1996), which are not considered here, rather than the more standard molecular electronic structure problem. It would therefore be relatively straightforward to make a computationally more efficient implementation than the one we use. In particular, we note that this code does not have linear molecule symmetry which means that calculations on LiH and CO had to be performed in C_{2v} and those on Li_2 used D_{2h}; the calculations on water used the natural C_{2v} symmetry of that system. All studies only considered the equilibrium geometry of each molecule.

Before considering our actual calculations in detail, it is worth briefly discussing what one should expect from them. At least for the ground state polarizabilities, the SOS method should give results which converge to the final answer for the given wavefunction and model monotonically from below. This behaviour is clearly illustrated by figures 1 and 2 which show convergence for particular cases presented below. The aim of the current study is to develop a

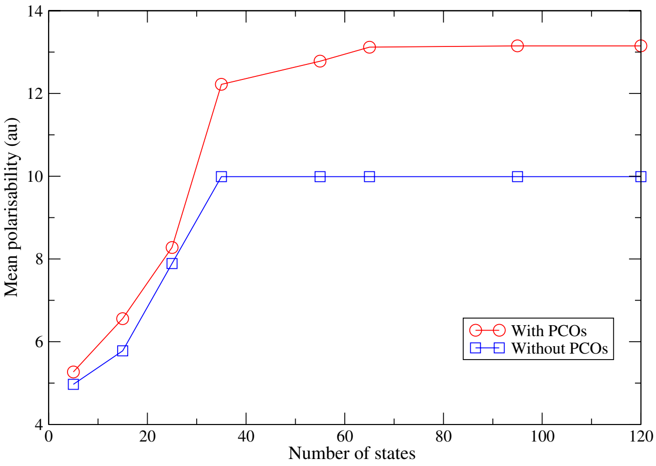

Figure 1. Convergence of the sum-over-states polarizabilty of CO using the HF model.

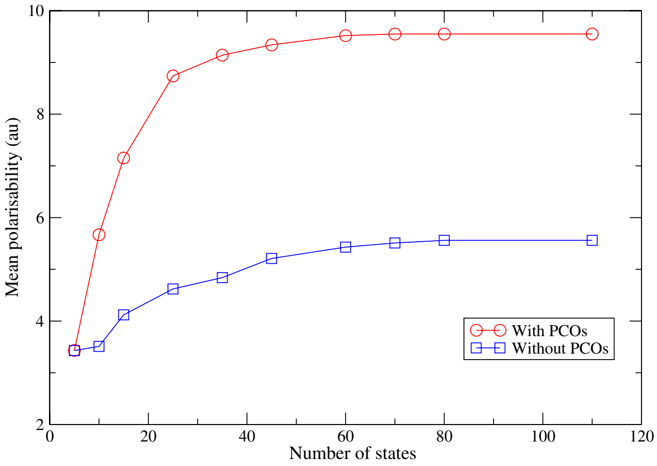

Figure 2. Convergence of the sum-over-states polarizabilty of water using a HF model for calculations with and without a pseudostate basis.

reliable method for obtaining the intrinsic polarizability of the given target wavefunction. If that wavefunction is exact, then the method should yield the observed polarizability within the constraint that we do not consider nuclear motion. However, with a less than perfect wavefunction one might expect, in general terms, that the intrinsic polarizability of that wavefunction will be larger than the true or observed polarizability. The reason for this is that biggest deficiency in most wavefunctions is in the treatment of the electron correlation problem. Increased electron correlation allows the wavefunction to shrink slightly making it more compact and less polarizable. It is possible, easy even, to get excellent agreement with observed polarizability due to a cancellation of errors: an incomplete SOS treatment counteracting an insufficiently correlated wavefunction. Below we have not invested huge computer resources to generate the best possible wavefunctions, such studies have been performed previously (Spelsberg and Meyer 1994, Jonsson *et al* 1996, Maroulis 1996, 1998, Junqueira and Varandas 2008). One would therefore expect the result of our converged SOS treatment to lead to a modest overestimation of the polarizability, at least for ground states. Bearing this in mind, we consider each system in turn.

3.1. LiH

LiH is a four-electron problem for which a large number of polarizabilty calculations are available, at least for the electronic ground state, see Bishop and Lam (1985) and Mérawa *et al* (2003), and references therein. For the ground state, we will benchmark our results against the high-accuracy calculations of Bishop and Lam (1985). Limited calculations are also available for the significantly larger polarizability of the A $^1\Sigma^+$ excited state of LiH, (Jonsson *et al* 1997, Mérawa *et al* 2003).

Tests were performed to assess the sensitivity of the calculations to choice of target models and pseudo-orbital basis set; these are only summarized below. In particular, a number of different basis sets were tested and the computed polarizabilities were found to depend quite strongly on this choice. For instance it was found that use of the basis set due to Sadlej (1988), although developed using the basis set polarization method to reproduce electronic properties of molecules, underestimated the polarizability of LiH by as much as 40%. However, the purpose of this paper is not to compare target wavefunctions, which has been done extensively previously (Jonsson *et al* 1996), and the calculations reported below all start from a cc-pVTZ basis (Dunning 1989). Tests at the Hartree–Fock level showed that the pseudo-orbital basis provides the significant extra polarization functions required to converge the polarizability at this level.

Going beyond Hartree–Fock wavefunctions, the LiH target states were represented using a complete active space (CAS) configuration interaction (CI) wavefunction; two different CAS–CI models were tested. For model A, the following configurations were used:

$$(1-6\mathrm{a}_1, 1-2\mathrm{b}_2, 1-2\mathrm{b}_1, 1-1\mathrm{a}_2)^4$$
$$(1-2\mathrm{a}_1)^3(\mathrm{PO})^1$$

where LiH target orbitals are labelled by their C_{2v} symmetry designations. Note that the second set of configurations means that all the pseudostates comprised states where three of the electrons were frozen in the lowest MOs. Model B is more flexible; it used the following configurations:

$$(1-6\mathrm{a}_1, 1-2\mathrm{b}_2, 1-2\mathrm{b}_1, 1-1\mathrm{a}_2)^4$$
$$(1-6\mathrm{a}_1, 1-2\mathrm{b}_2, 1-2\mathrm{b}_1, 1-1\mathrm{a}_2)^3(\mathrm{PO})^1$$

which clearly allows all configurations to generate associated pseudostates. With 25 a_1, 12 b_1, 12 b_2 and 6 a_2 POs, model A gave 376 configurations of $^1A_1$ symmetry while model B gave 2856. These models gave a total electronic energy of -7.9901 and -8.0015 E_h respectively, which can be compared to a high-accuracy value of -8.0206 E_h (Roos and Sadlej 1982).

The nature of the PO basis was investigated by (a) varying the chosen values of ζ_0 and β, (b) varying the size of the PO basis and (c) varying the deletion threshold, δ. It was found that reducing the size of the PO basis below the (25,12,12,6) set discussed above led to an underestimate in the calculated

Table 1. Polarizability of LiH (in au): comparison of different PO basis sets and target models, see the text for details.

Model	ζ_0	β	$\alpha_\perp$	$\alpha_\parallel$	$\overline{\alpha}$
A	Without POs		7.01	9.32	7.78
A	0.10	1.2	34.22	29.08	32.51
A	0.13	1.3	33.81	26.89	31.51
A	0.15	1.5	32.55	25.65	30.25
A	0.18	1.3	31.83	25.62	29.76
B	0.18	1.3	29.76	26.92	28.81
	Accurate values[a]		29.76	26.36	28.63

[a] *Ab initio* values from Bishop and Lam (1985).

Table 2. Polarizability (in au) of the A $^1\Sigma^+$ state of LiH.

	$\alpha_\parallel$	$\alpha_\perp$	$\overline{\alpha}$
This work	59.50	197.67	151.61
Mérawa *et al* (2003)	57.69	177.27	137.41

polarizability, but increasing it by extending the geometric series, which has the effect of adding extra tight functions to the basis, made only negligible difference. Furthermore, the calculations are insensitive to values of δ between 2×10^{-7} and 2×10^{-5}, the usual range of this parameter; the higher value was used for the results reported.

A range of ζ_0 and β combinations were tested, a selection of which are shown in table 1; $\zeta_0 = 0.18$ and $\beta = 1.3$ was found to give the best results. When no pseudostates are used, the SOS method underestimates the intrinsic polarizability of the wavefunction, giving only about 25% of the real value. The pseudostates method gives values which reflect the true polarizability of the system. With model A, the calculated polarizabilities are somewhat too large; the difference compared with the accurate theoretical value of Bishop and Lam (1985) is reduced significantly on using model B. One would expect this difference to continue to reduce as the target wavefunction is improved.

Turning to the A $^1\Sigma^+$ excited state of LiH, table 2 summarizes the results of our calculations and makes comparison with the previous study. Our calculations are based on the use of model A which gave a vertical excitation energy from the ground state of 3.36 eV, in good agreement with the calculated, 3.20 eV, and measured, 3.29 eV, values given by Jonsson *et al* (1996).

We could find only two previous calculations of the polarizability of the A$^1\Sigma$ state of LiH in the literature. Table 2 compares the polarizability of the A$^1\Sigma$ state calculated by us using $\zeta_0 = 0.18$ and $\beta = 1.3$ with the value of Mérawa *et al* (2003) who used a time-dependent gauge invariant approach. We note that although Jonsson *et al* (1996) performed the cubic response calculations on the dynamic polarizability of the A$^1\Sigma$ state of LiH, they did not give a field-free value for us to compare with. Table 2 shows that the parallel component found using the pseudo-states method is in good agreement with the only previously published value found. However, our calculation appears to overestimate the perpendicular polarizability. An improved excited state wavefunction would be needed to reduce this value.

Table 3. Number of MOs and POs retained in each model for Li_2; orbitals are labelled by the irreducible representations of D_{2h}; numbers for b_{3u} and b_{3g} are the same as b_{2u} and b_{2g} respectively.

Model	type	a_g	b_{2u}	b_{1g}	b_{1u}	b_{2g}	a_u
PO1	MOs	9	4	1	6	4	1
	POs	20	9	5	11	7	1
PO2	MOs	7	3	1	3	4	1
	POs	15	6	5	5	4	1

3.2. Li_2

The lithium dimer is unusual in the large size of its ground state polarizability; as will be seen it is also unusual in its SOS behaviour in that both the parallel and perpendicular polarizabilities are dominated by excitation to the first excited state of the appropriate symmetry. Li_2 was recently the subject of successful RMPS by Tarana and Tennyson (2008). Some of the features of the present calculation are copied from that work.

Calculations were performed with a cc-pVDZ basis set (Dunning 1989). The target state configurations for Li_2 were generated using CAS–CI wavefunctions, following Tarana and Tennyson (2008) in which the four 1s core electrons were frozen and all symmetry-allowed configurations which involved exciting one valence electron were retained. The pseudostates were generated using single excitations from this CAS.

The extended nature of the Li_2 wavefunction means that the PO basis must be much more diffuse than for most systems. Two PO basis sets with low values for ζ_0 were tested, following Tarana and Tennyson (2008); PO1 used $\zeta_0 = 0.052$ and PO2 the more diffuse 0.0463. The deletion threshold in the orthogonalization between the POs and target MOs was set to 2×10^{-2} to reduce the size of the calculation, although use of δ as low as 2×10^{-7} also gave stable results. The number of MOs and POs retained in each model is given in table 3.

Table 4 shows the effect of different SOS expansions and PO models on the polarizability. Including only the first excited state in the SOS recovers over 96% of $\alpha_\perp$ and a remarkable 98% of $\alpha_\parallel$. A consequence of this behaviour is that the Hartree–Fock model, which is known not to give reliable target excitation energies, yields relatively poor values for the polarizabilities; our calculations gave $\alpha_\perp = 218.57$ au and $\alpha_\parallel = 296.09$ au. Conversely convergence of the SOS is rapid and there appears to be little need to consider continuum effects for the system. Indeed, while two pseudostate models give very similar values for the polarizabilities, the SOS expansion for a CAS–CI calculation without pseudostates actually converges very rapidly to a slightly higher value. This behaviour is in marked contrast to the final two systems considered.

3.3. CO

The construction of the target state configurations is more complicated for CO than the few-electron molecules discussed above, as there are many more possible target models. The models used here are summarized in table 5. The simplest

Table 4. Li_2 ground state polarizabilities (in au) for various models based on the CAS–CI target wavefunction described in the text. The number of states refers to respectively the number of states of symmetry $^1B_{2u}$ and $^1B_{1u}$ retained in the SOS expansion.

PO model	Number of states $^1B_{2u}$	Number of states $^1B_{1u}$	$\alpha_\perp$	$\alpha_\parallel$	$\overline{\alpha}$
None	5	5	160.587	317.374	212.85
None	15	15	160.588	317.374	212.85
PO1	1	1	155.20	309.44	206.61
PO1	45	75	160.54	315.68	212.51
PO2	1	1	154.95	309.44	206.45
PO2	11	11	160.19	315.28	211.89
PO2	45	75	160.50	315.73	212.24
Accurate values[a]			160	303	208

[a] *Ab initio* values of Mérawa and Rérat (2001).

Table 5. CO target configurations used in the present calculations; orbitals are labelled using the C_{2v} point group.

Target model	Configurations
HF	$(1a_1, 2a_1, 3a_1, 4a_1, 5a_1, 1b_2, 1b_1)^{14}$ $(1a_1, 2a_1, 3a_1, 4a_1, 5a_1, 1b_2, 1b_1)^{13}$ (PO)^1
CAS1	$(1a_1, 2a_1)^4(3a_1, 4a_1, 5a_1, 1b_2, 2b_2, 1b_1, 2b_1)^{10}$ $(1a_1, 2a_1)^4(3a_1, 4a_1, 5a_1, 1b_2, 2b_2, 1b_1, 2b_1)^9$ (PO)^1
CAS2	$(1a_1, 2a_1, 3a_1)^6(4a_1, 5a_1, 1b_2, 2b_2, 1b_1, 2b_1)^8$ $(1a_1, 2a_1, 3a_1)^6(4a_1, 5a_1, 1b_2, 1b_1)^7$ (PO)^1

model used was a Hartree–Fock (HF) target in which all electrons are frozen and only one configuration is generated; for this model pseudostates were generated by considering single excitations from each orbital. This means, unlike the models considered below, that polarization of the core electrons is explicitly allowed for. In our larger CAS model, CAS1, the two lowest MOs are kept doubly occupied freezing the four 1s electrons and the remaining ten electrons are freely distributed in the 3–5a_1, 1–2b_2 and 1–2b_1 orbitals. In CAS2, the three lowest MOs were kept doubly occupied. CAS2 was investigated as it is computationally cheaper than CAS1 but should give similar results as the behaviour of the outer electrons should dominate the polarizability.

The basis set used in this calculation was the augmented triple zeta atomic natural orbital basis due to Widmark *et al* (1990). This is a relatively large basis set; other smaller basis were investigated such as the cc-pVTZ but it was found that these smaller basis sets underestimated the parallel component of the polarizability. The number of MOs (and POs) used in the calculation in each of the irreducible representations of the C_{2v} point group were $a_1 = 7(31)$, $b_2 = 5(20)$, $b_1 = 5(20)$, $a_2 = 1(7)$. Reducing the number of MOs resulted in the polarizability being underestimated.

For CO a wide range of PO basis sets were investigated. Our basic set used POs with $l \leqslant 2$ comprising (10s, 10p, 6d); use of $l \leqslant 1$ was found to underestimate the polarizability and $l \leqslant 3$ gave no significant change to the results, as might be expected for a system with no occupied d orbitals. Table 6 shows the results for different values of ζ_0 and β and HF model. As a starting point values of $\zeta_0 = 0.14, 0.15, 0.16, 0.17$ and $\beta = 1.3$ were taken from Gorfinkiel and Tennyson (2004). These values gave accurate results. Higher and lower values of ζ_0 and β were then investigated; it was found that slightly increased values such as $\zeta_0 = 0.18$ or $\beta = 2.3$ do not materially affect these results. It is only when these numbers were increased or decreased by larger amounts that the estimated polarizabilities dropped. With the lower values of β, it was necessary to raise the deletion threshold, as basis sets with low values of β make it harder to avoid linear dependence.

Table 6. Effect of PO basis on the calculated polarizability (in au) of CO using an HF target wavefuntion.

α_0	β	$\alpha_\perp$	$\alpha_\parallel$	$\overline{\alpha}$
0.15	1.1	11.76	15.61	13.04
0.15	1.3	11.71	15.80	13.07
0.15	2.3	11.45	15.43	12.78
0.15	6.1	10.83	12.92	11.53
0.14	1.3	11.66	15.83	13.05
0.18	1.4	11.64	15.66	12.98
0.92	1.3	9.46	13.07	10.66
0.0056	1.3	10.01	12.11	10.71
0.25	1.3	11.49	15.39	13.24
Accurate values[a]	11.99	15.73		

[a] *Ab initio* values of Junqueira and Varandas (2008).

Table 7. Polarizability (in au) of CO using various models, see text for details.

Target configuration	$\alpha_\perp$	$\alpha_\parallel$	$\overline{\alpha}$
No POs	9.38	10.94	9.90
HF	11.66	15.83	13.05
CAS1	12.34	15.29	13.32
CAS2	12.78	15.49	13.68
Accurate value[a]	11.99	15.73	13.24
Experimental[b]	12.15	15.72	13.34

[a] *Ab initio* results of Junqueira and Varandas (2008).

[b] Measured value for the $v = 0$ state of CO (Bridge and Buckingham 1966).

Figure 1 shows the convergence of the SOS expression for calculations with and without POs. This figure shows that about 60 states are required to converge the pseudostate calculation, which was also found to be sufficient for the larger CAS model. It also shows that the more rapidly convergent non-pseudostate calculation only recovers about 70% of the polarizability.

Calculations using CAS1 and CAS2 models are more computationally expensive than those with the HF target. While the HF model gives 180 configurations of $^2A_1$ symmetry, CAS1 generates over 10 000 and CAS2 generates 313. Table 7 shows the calculated polarizabilities as a function of model. These results are compared with the accurate *ab initio* values of Junqueira and Varandas (2008). The experimental values of Bridge and Buckingham (1966) are also given for comparison, although it should be noted that vibrational effects are responsible for most of the difference between our CAS calculations and these values, so a direct comparison is not very illuminating. The agreement with the results of Junqueira and Varandas (2008) is good. We

Table 8. Excited state polarizability (in au) of CO A $^1\Pi$.

Model	α_{zz}	α_{xx}	α_{yy}	$\overline{\alpha}$
This work, HF	19.79	16.26	16.26	17.43
Jonsson *et al* (1997), HF	21.62	20.15	19.53	20.44
Jonsson *et al* (1997), CAS	18.78	22.43	14.69	18.63

note, rather unusually, that the value of $\alpha_\perp$ increases upon the inclusion of correlation before decreasing again.

We also investigated the polarizability of the first two excited states of CO: the A $^1\Pi$ and a $^3\Pi$ states. For the singlet state the HF target, used previously for the ground state calculation, was used, although the dipole transition rules mean that coupling to states of $^2A_2$ symmetry also have to be considered. The same number of MOs were selected, although fewer POs were available due to the different PO basis. Values of $\zeta_0 = 0.10$ and $\beta = 1.2$ were used to generate the PO basis. The only values for the polarizability of the A $^1\Pi$ state that could be found in the literature were from Jonsson *et al* (1996) using cubic response functions and the finite field method.

Table 8 shows that the α_{zz} and α_{yy} components and the mean polarizability are in reasonable agreement with the values of Jonsson *et al* (1996). It is unclear why the α_{xx} component of Jonsson *et al* differs from their α_{yy} component for the same model. As with the ground state of CO, the polarizability is found to converge to these values with around 60 states per symmetry.

For the a $^3\Pi$ state different target configurations were generated, and due to the different spin of the triplet state, unpaired electrons had to be included in the target configuration. The target CAS model used was based on the following configurations:

$$(1a_1, 2a_1, 3a_1, 4a_1)^8(5a_1, 1b_2, 2b_2, 1b_1, 2b_1)^6$$
$$(1a_1, 2a_1, 3a_1, 4a_1)^8(5a_1, 1b_2, 2b_2, 1b_1, 2b_1)^5\ (\mathrm{PO})^1.$$

No values for the a $^3\Pi$ state polarizabilities could be found in the literature. Using the pseudo-states method gives $\alpha_\perp = 14.39$, $\alpha_\parallel = 24.61$ and $\overline{\alpha} = 17.80$ au, similar to the values found for the A $^1\Pi$ state.

3.4. Water

For H_2O two target models were investigated: a HF target, in which all ten electrons were frozen in the lowest MOs, and a CAS. With a PO basis, the HF model gives

$$(1a_1 2a_1 3a_1 1b_2 1b_1)^{10}$$
$$(1a_1 2a_1 3a_1 1b_2 1b_1)^9\ (\mathrm{PO})^1.$$

The CAS model froze the oxygen 1s and 2s electrons giving

$$(1-2a_1)^4\ (3-4a_1, 1-2b_2, 1-2b_1)^6$$
$$(1-2a_1)^4\ (3-4a_1, 1-2b_2, 1-2b_1)^5\ (\mathrm{PO})^1$$

which gives 8001 configurations of $^1A_1$ symmetry.

For the H_2O calculations the choice of target basis set did not have a large effect on the results: double, triple and quadruple zeta basis sets were tested with only small variation in the results; both Maroulis (1998) and Junqueira and Varandas (2008) present extensive studies on the sensitivity to different basis sets. Results for a cc-pVTZ basis set are presented below. Table 9 gives the number of orbitals used in the two models considered.

Table 9. The number of MOs and POs retained $\zeta_0 = 0.15$ and $\beta = 1.3$ in the calculation for each irreducible representations of C_{2v}.

		a_1	b_2	b_1	a_2
HF	MOs	6	4	4	2
	POs	32	17	17	7
CAS	MOs	26	18	18	3
	POs	40	25	25	6

Table 10. Polarizabilities of H_2O (in au) using different models.

Model	α_{xx}	α_{yy}	α_{zz}	$\overline{\alpha}$
HF	10.37	8.43	9.53	9.42
CAS	9.99	8.66	9.05	9.24
Accurate values				
HF (Jonsson *et al* 1997)	9.16	8.45	7.81	8.47
CAS (Jonsson *et al* 1997)	9.64	9.20	8.92	9.25
CBS (Junqueira and Varandas 2008)[a]	9.95	9.68	9.47	9.70
Measured[b]	9.68	9.47	9.19	9.45

[a] Complete basis set extrapolated values.
[b] Best available experimental value, see John *et al* (1980), as corrected for zero point energy effects (Jonsson *et al* 1997).

As before, different values of ζ_0 and β were investigated; it was found that $\zeta_0 = 0.15$ and $\beta = 1.3$ gave the best results. 10s, 10p and 6d functions were used in the PO basis; again using s and p functions only resulted in underestimated polarizabilities, while using $l \geqslant 3$ increased the time taken to complete the calculation without significantly changing the results. The same was found when the number of POs was increased, for example when 20s, 20p and 11d functions were used. Figure 2 shows the convergence of the calculation with the SOS. As with CO, the use of pseudostates to represent a discretized version of the electronic continuum is essential for convergence to accurate values: without them only about half the polarizability is recovered. With pseudostates, the mean polarizability converges to accurate values in 45 states per ($^1A_1$, $^1B_2$ and $^1B_1$) symmetry.

As shown in table 9, the CAS model requires more MOs and POs; using less orbitals than this resulted in underestimated values of the polarizability. In this case it was found that using slightly more diffuse basis with $\zeta_0 = 1.2$ and $\beta = 1.2$ gave the highest results.

Table 10 shows the polarizabilies for H_2O calculated using the two target models. Due to the geometry of the H_2O molecule, the polarizability is almost isotropic; this is found in all works quoted. The excellent agreement between our HF calculation and the experimental value for the mean polarizability, which is corrected for the effects of vibrational motion (Jonsson *et al* 1997), must be regarded as fortuitous. As expected, inclusion of correlation leads to a general reduction in our calculated polarizabilities; why this is not so for the calculations of Jonsson *et al* (1997) is unclear.

4. Conclusions

We demonstrate the ability of an even-tempered basis located on the centre of molecular mass to generate converged sum-over-state (SOS) polarizabilities for a variety of small molecules. Although the idea for this treatment arose from *R*-matrix studies (Allison *et al* 1972, Gorfinkiel and Tennyson 2004), the only link with the *R*-matrix procedure is conceptual. As in the *R*-matrix method, the procedure is based on getting a basis set representation of the continuum in the geometric region occupied by the target wavefunction of interest. Although our calculations used an *R*-matrix code, these calculations can be performed with any suitable adapted *ab initio* program suite.

Our proposed method uses an extra basis set located at the molecular centre-of-mass. It is of course possible to get a, perhaps partial, representation of the continuum using large, atom-centred basis sets. However, the even-tempered basis we use has significant advantages in terms of systematic coverage and completeness. Furthermore, although we performed tests for relatively small atomic basis sets, the method is equally applicable to calculations which use a large atom-centred basis set. In this case it is to be expected that rather more functions will be removed by the orthogonalization procedure we outline; however, this procedure is robust and we do not anticipated any extra difficulties arising in this case.

A disadvantage of the SOS method is the potentially large number of states that can be generated once sophisticated, i.e. correlated, target wavefunctions are used. Our numerical tests showed that for the problems we studied typically a few tens of states, 60 or less, are sufficient to get well-converged polarizabilities; similar observations have been made for *R*-matrix calculations (Tennyson 2004). In one extreme case, that of the very polarizable Li_2 molecule, it seems that it is not necessary to consider the continuum at all.

Junqueira and Varandas (2008) also recently explored completeness with respect to the calculation of molecular polarizabilities. Their method, and indeed their focus, was somewhat different from ours but the comparison is interesting. Junqueira and Varandas used basis set extrapolation of large CI calculations to converge both their wavefunctions and their polarizabilities which they calculated using a finite field technique. They observe that the advantage of this technique is that only the ground state energies are required but a serious drawback is that it cannot be extended to calculate dynamic polarizabilities.

A drawback of the pseudostate method applied here is that it requires the knowledge of many excited states which are required for the calculation of the dipole couplings. Conversely, the pseudostate method can be extended to calculate dynamic polarizabilities in a straightforward fashion (Allison *et al* 1972) by generalizing equation (1):

$$\alpha_{rs}(\omega) = 2\sum_{n>0}(E_n - E_0)\frac{\langle 0|\mu_r|n\rangle\,\langle n|\mu_s|0\rangle}{(E_n - E_0)^2 - \omega^2} \qquad (3)$$

where ω is the frequency of interest. This is a significant advantage of our proposed method.

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