CSIRO PUBLISHING

Australian Journal of Physics

Volume 51, 1998 © CSIRO 1998

A journal for the publication of original research in all branches of physics

www.publish.csiro.au/journals/ajp

All enquiries and manuscripts should be directed to Australian Journal of Physics CSIRO PUBLISHING PO Box 1139 (150 Oxford St) Collingwood Telephone: 61 3 9662 7626 Vic. 3066 Facsimile: 61 3 9662 7611 Australia Email: peter.robertson@publish.csiro.au



Published by **CSIRO** PUBLISHING for CSIRO and the Australian Academy of Science



A Procedure to Determine Dyson Orbitals from Electron Momentum Spectroscopy: Application to 1,2-Propadiene, 1,3-Butadiene, Cyclopropane and [1.1.1]Propellane*

R. J. F. Nicholson,^A I. E. McCarthy and M. J. Brunger

Department of Physics, Flinders University of South Australia, GPO Box 2100, Adelaide, SA 5001, Australia. phmjb@cc.flinders.edu.au ^APresent address: Land Operations Division, PO Box 1500, Salisbury, SA 5018, Australia.

Abstract

We employ a numerical inverse method of extracting the target–ion overlap, or normalised Dyson orbital, directly from experimental electron momentum spectroscopy data by using a quantum-mechanically constrained statistical fitting procedure. This method is used in conjunction with the previously verified, for molecular targets, plane wave impulse approximation (PWIA) reaction model. The present procedure was applied to previously measured momentum distributions (MDs) for the 2e' and 1e' valence orbitals of cyclopropane, the 7ag orbital of trans 1,3-butadiene, the 2e orbital of 1,2-propadiene and the 3a'_1 orbital of [1.1.1]propellane. We note that this is the first extensive application of the present method to organic molecular systems. In each case the derived normalised Dyson orbital provided a superior representation of the experimental MD than did the corresponding Hartree–Fock orbital. The ramifications of this result are discussed in the text.

1. Introduction

A great deal of our knowledge pertaining to atomic, molecular, nuclear and particle physics is information gathered from scattering experiments. Inferring the structure of systems involved in the experiment or what is the interaction between the particles, from the data measured in the scattering experiment, is the so-called inverse problem. The quantum mechanical inverse scattering procedure is a problem of long standing, the status and extent of the field being well summarised in the review of Chadan and Sabatier (1989).

Of particular relevance to us is its development for application in electron-atom and electron-molecule (Lun *et al.* 1994) scattering processes. Inverse scattering techniques were first applied to electron-atom scattering by Bürger *et al.* (1983) who used both fully quantal (Lipperheide and Fiedeldey 1978, 1981) and semiclassical WKB (Allen and Burger 1984) inversion methods to obtain phase-shifts and then local potentials for e–He scattering, from elastic cross section data (Andrick and Bitsch 1975) for incident energies of 2 and 19 eV. These potentials, obtained without any *a priori* assumptions about their analytic form, were in agreement with our physical expectations both in the tail and at short range. Namely, the incoming electron sees a polarisation potential at large distances

* Dedicated to Professor Erich Weigold on the occasion of his sixtieth birthday.

© CSIRO Australia 1998

```
10.1071/PH97065
```

0004-9506/98/040691\$05.00

and the Coloumb potential due to the nuclear protons at small distances. There is also a weak energy dependence of the local potential at intermediate distances which is a manifestation of the non-local exchange interaction.

Further developments to the quantum mechanical inversion procedure have been made by Leeb *et al.* (1985), Allen (1986), Allen and McCarthy (1987), Allen *et al.* (1987), Brunger *et al.* (1992) and Buckman *et al.* (1998), to whom the reader is referred for further detail.

The process we apply is the exact analogue of the phase-shift analysis discussed above for an atomic elastic-scattering experiment. We apply it to a kinematically-complete ionisation experiment that is considered as a probe for observing the Dyson orbitals of electrons in a molecule. This is electron momentum spectroscopy (EMS). We employ a numerical inverse statistical fitting method to unravel the probe properties from the experimental EMS data, thereby exposing the Dyson orbital. The Dyson orbital is described by a finite set of parameters, which we choose conveniently as an overall scaling factor, necessitated by the fact that absolute (e, 2e) cross sections are not determined experimentally, and the coefficients of a linear combination of orthonormal orbitals of the required symmetry. The parameter fit is constrained by the requirement that all the resulting orbitals must be orthonormal. This procedure, which is described in more detail in the next section, is adapted from a method used by Weyrich and colleagues (Schmider et al. 1990, 1992, 1993) for the reconstruction of density matrices from Compton scattering data. We note that the present study reports results for its first extensive application to organic molecular systems.

There are several aspects for the use of the orbitals determined by the fitting procedure. Firstly, as they constitute a large fraction of the information that characterises electronic structure, they can be used to derive the chemically interesting molecular property information for the molecule in question. Furthermore, in principle, this molecular property information should be more accurate than that correspondingly obtained from the Hartree–Fock basis. Secondly, the method is also a way of checking the model used for the reaction mechanism.

In the next section we give brief details for the plane wave impulse approximation (PWIA) reaction mechanism and a somewhat more detailed account of the inversion procedure. In Section 3 a brief description of the experimental momentum distributions (MDs) used in the present analysis is provided. Our results and a discussion of them are given in Section 4 with conclusions being drawn in Section 5.

2. Reaction Mechanism and Inversion Procedure Details

A full description of the PWIA reaction model, the weak-coupling approximation, Dyson orbitals and the inversion procedure, all of which are relevant to this study, can be found in Nicholson *et al.* (1998). Nonetheless, to ensure the present article is to a large degree self-contained, a precis of the discussion in Nicholson *et al.* (1998) is now presented.

EMS measures the momentum distribution $\sigma_i(q)$ for states *i* of the residual ion in an ionisation reaction where the measured incident and two outgoing electron momenta are \mathbf{k}_0 , \mathbf{k}_A , \mathbf{k}_B and

$$\boldsymbol{q} = \boldsymbol{k}_A + \boldsymbol{k}_B - \boldsymbol{k}_0 \,, \tag{1}$$

where q is the recoil momentum of the target.

For molecular targets in the kinematic range relevant to EMS there is now a large body of evidence (McCarthy and Weigold 1991; Brion 1992) supporting the conclusion that the PWIA gives a quantitative relationship between the measurements and the target-ion structure, represented by the electronic ground states 0 of the target and i of the ion. We assume this validity of the PWIA description for the reaction mechanism in this study.

The PWIA is

$$\sigma_i(q) = (2\pi)^4 \frac{k_A k_B}{k_0} f_{ee}(4\pi)^{-1} \int d\hat{\boldsymbol{q}} |\langle \boldsymbol{q} i | 0 \rangle|^2 , \qquad (2)$$

where the structure amplitude is defined by

$$\langle \boldsymbol{q}i|0\rangle = \langle \boldsymbol{k}_A \boldsymbol{k}_B \ i|0\boldsymbol{k}_0\rangle \tag{3}$$

and f_{ee} is the e-e collision factor which, in noncoplanar symmetric kinematics, is essentially independent of momentum up to about 2 a.u. at $E_0 = 1000$ eV. Note that within the PWIA framework $-\boldsymbol{q} = \boldsymbol{p}$, where \boldsymbol{p} is the momentum of the struck electron at the instant of ionisation. Further, note that experimentally we vary \boldsymbol{p} by varying the out-of-plane azimuthal angle ϕ (see McCarthy and Weigold 1991).

Further understanding of the structure amplitude comes from defining an appropriate set of target orbitals. Note that $\langle \mathbf{q}i|0\rangle$ is a one-electron function, the Dyson orbital. It is useful to define a normalised Dyson orbital α by the weak-coupling approximation (Nicholson *et al.* 1998),

$$\langle \boldsymbol{q}i|0\rangle = (S_i^{\alpha})^{\frac{1}{2}} \langle \boldsymbol{q}|\alpha\rangle, \qquad (4)$$

which assigns certain states i to an orbital manifold α , identified by identical shapes of the momentum profiles for all $i \in \alpha$, characteristic of the orbital α . Here S_i^{α} is the spectroscopic factor. Orbital manifolds are identified in all EMS. They are due to the splitting of the one-hole ion state $\bar{\alpha}$, obtained by annihilating an electron in the target orbital α , which is occupied in the independent-particle configuration, by ion-state correlations. The correlations are described in a configuration-interaction representation by admixtures of determinantal configurations found by excitation of particles and holes in the independent-particle configuration.

The momentum distribution is

$$\sigma_i(q) = (2\pi)^4 \frac{k_A k_B}{k_0} f_{ee} (4\pi)^{-1} S_i^\alpha \int d\hat{\boldsymbol{q}} |\langle \boldsymbol{q} | \alpha \rangle|^2 \,.$$
(5)

The intensity for states $i \in \alpha$ is proportional to S_i^{α} .

The weak-coupling approximation is confirmed experimentally by verifying two of its consequences. These are the spectroscopic sum rule for manifold α

$$\sum_{i} S_i^{\alpha} = 1 \tag{6}$$

and the similarity of momentum profile shapes for the states $i \in \alpha$. In almost all known cases the hypothesis that the relative normalisation of states $i \in \alpha$ is given by the spectroscopic factor is confirmed by identifying enough states i to exhaust the sum rule (equation 6) for different manifolds, which are then compared.

Until recently EMS analysis was performed in terms of orbitals obtained from self-consistent-field (SCF) calculations of the target structure. In a fair number of cases these orbitals were sufficient to describe profile shapes, but glaring exceptions are known, for example the 1π manifold of hydrogen fluoride (Braidwood *et al.* 1993), which is essentially a one-state manifold but is not well described by a Hartree–Fock orbital. Neither is it well described, for that matter, by a local density approximation (LDA) level density-functional calculation (Duffy *et al.* 1994).

Here we consider the experiment as a probe for the normalised Dyson orbital $\langle \boldsymbol{q} | \alpha \rangle$ and we ask what function the experiment yields as an estimate of this orbital. The data from the spectroscopic experiment to be used for the inversion procedure consist of the ionisation cross section for the states *i* of the α orbital manifold at data points $\mu \equiv (\hat{k}_A, \hat{k}_B)$, summed for a subset of these states in the spirit of equation (4). Before doing the summation one can test the validity of (4) by verifying the MDs have the same shape for all *i* $\epsilon \alpha$. One overall multiplicative constant is undetermined by the EMS experiment. The absolute outgoing momenta k_A and k_B are fixed. The numerical inversion procedure is designed to unravel a single normalised Dyson orbital or an orthonormal set of such orbitals from the MD data and is based on formulating it in terms of the reconstruction of a quasiparticle density matrix (Nicholson *et al.* 1998).

For that purpose a normalised Dyson orbital α is expressed as a linear combination of M^{τ} orthonormal basis orbitals β , whose symmetry τ is the same as α , but whose principal quantum numbers are different,

$$|\alpha\rangle = \sum_{\beta=1}^{M^{\tau}} |\beta\rangle C_{\beta\alpha} \,. \tag{7}$$

(8)

The experimental situation in the measurement of the (e, 2e) cross sections (MDs) σ^{α}_{μ} (e, 2e) [data points (α, μ) belonging to $|\alpha\rangle$ at momentum q_{μ}] is simulated by including a description of the angular resolution in the theoretical cross section σ^{α}_{μ} . In the experimental conditions used for this spectroscopy the finite energy acceptance has no effect. The theoretical cross section (equation 5) is integrated over normalised weight factors W_A and W_B for \hat{k}_A and \hat{k}_B ,

$$\begin{aligned} \sigma^{\alpha}(q_{\mu}) &= \sigma^{\alpha}_{\mu} \\ &= (2\pi)^4 \frac{k_A k_B}{k_0} f_{ee}(4\pi)^{-1} S^{\alpha}_i G \int d\hat{\boldsymbol{q}} \int d\hat{\boldsymbol{k}} W_A(\hat{\boldsymbol{k}}, \hat{\boldsymbol{k}}_A) \int d\hat{\boldsymbol{k}}' W_B(\hat{\boldsymbol{k}}', \hat{\boldsymbol{k}}_B) |\langle \boldsymbol{q} | \alpha \rangle|^2 \,, \end{aligned}$$

which can conveniently be written as

$$\sigma^{\alpha}_{\mu} = (2\pi)^4 \frac{k_A k_B}{k_0} f_{ee}(4\pi)^{-1} F^{\alpha} \int d\hat{\boldsymbol{q}} \int d\hat{\boldsymbol{k}} W_A(\hat{\boldsymbol{k}}, \hat{\boldsymbol{k}}_A) \int d\hat{\boldsymbol{k}}' W_B(\hat{\boldsymbol{k}}', \hat{\boldsymbol{k}}_B) |\langle \boldsymbol{q} | \alpha \rangle|^2 \,. \tag{9}$$

The constant F^{α} in equation (9) is not measured by the experiment and is treated as a fitting parameter. It is made up of a factor G due to the experimental conditions and the sum S^{α} of spectroscopic factors appropriate to the states of the orbital manifold that have been summed up in the experimental data. If all the states are included, this sum is 1. The same experiment may determine data for more than one orbital manifold. In this case the factor G is the same for each, so that S^{α} is determined for each orbital manifold relative to the others.

The criterion for the best choice of the parameters $(C_{\beta\alpha}, F^{\alpha})$ is minimisation of the weighted-least-squares functional χ^2 , defined by

$$\chi^{2} = \sum_{\mu,\alpha} W^{\alpha}_{\mu} [\sigma^{\alpha}_{\mu}(\mathbf{e}, 2\mathbf{e}) - \sigma^{\alpha}_{\mu}]^{2} , \qquad (10)$$

where σ^{α}_{μ} is given by equation (9). The normalised weight W^{α}_{μ} of each experimental datum point (α, μ) is the inverse of the variance for (α, μ) (see Bevington and Robinson 1992). Taylor expansion of the first partial derivatives of χ^2 with respect to the parameters and cut-off after terms linear in the parameter variations lead to the Gaussian normal equations to be solved iteratively for these variations. For the purpose of the density-matrix reconstruction in the extraction of atomic orbital information from Compton profiles (Schmider *et al.* 1990, 1992, 1993) it has turned out to be important to stabilise and to accelerate convergence by inclusion of the terms quadratic in the parameter variations. In all of the examples to be shown in the present paper fast convergence could thus be obtained.

The errors on the determined parameters $C_{\beta\alpha}$ and F^{α} were found in a numerically valid way by adapting the $\Delta\chi^2 = 1$ procedure of Bevington and Robinson (1992) to the present application. A full discussion of this approach can be found in Bevington and Robinson, to whom the reader is referred for details.

The fitting is constrained by the unitarity of the transformation matrix $C_{\beta\alpha}$, which ensures that the resulting orbitals are orthonormal. The unitarity constraint is achieved by parametrising the coefficients with the set of Jacobi-type planar rotation matrices $R(\theta_j)$, which have the same dimensions as $C_{\beta\alpha}$. The set θ of fitting parameters comprises the rotation angles θ_j and the normalisation constraint F^{α} . More details on this can be found in Nicholson *et al.* (1998). Each fit determines M^{τ} orbitals α , including the ones relevant to the data fitted.

3. Momentum Distribution Measurements

All of the molecular MDs employed in conjunction with the current analysis were measured with an EMS spectrometer (McCarthy and Weigold 1991) in symmetric non-coplanar configuration ($\theta_A = \theta_B = 45^\circ$; $E_A = E_B$). The 2e MD of 1,2-propadiene was measured at a total energy of 1500 eV and originally reported in the work of Braidwood *et al.* (1994), to which the reader is referred for details of the experimental measurements. Similarly, the 2e' and 1e' MDs of cyclopropane were also measured at a total energy of 1500 eV. In this case full details of the experiment can be found in von Niessen *et al.* (1994). The measurement for the $3a'_1$ MD of [1.1.1]propellane is discussed in detail by Adcock *et al.* (1997). Here, however, the total energy is now 1000 eV. Finally, a full description of the technique employed in the measurement of the $7a_q$ MD of trans 1,3-butadiene is reported in the recent paper of Brunger *et al.* (1998). We note that the total energy in this study was once again 1500 eV.

The experimental MDs considered were chosen for a variety of reasons. These included the ease of availability of the Flinders data over that from other groups, the fact that in the respective binding energy spectra for the different molecules the chosen orbitals were always quite well resolved from their nearest neighbours and, whilst two of the organic species (1,2-propadiene and trans 1,3-butadiene) were representative of the -diene family of compounds, the latter being a good example of a conjugated -diene, the remaining molecules (cyclopropane and [1.1.1]propellane) are excellent examples of highly-strained systems. In addition, we had previously seen (Braidwood et al. 1994; von Niessen et al. 1994) that the respective Hartree–Fock orbitals for the 2e state of 1,2-propadiene and the 2e' state of cyclopropane did not give a very good representation of the relevant measured MDs. Note that as the 1e' orbital of cyclopropane is of the same symmetry as the 2e' orbital it was included in the present study to specifically investigate the orthonormality constraint in the parameter fit. Finally, as the respective Hartree–Fock level orbitals gave reasonable representations for the $3a'_1$ MD of [1.1.1] propellane (Adcock *et al.* 1997) and $7a_g$ MD of butadiene (Brunger et al. 1998) they were included to see whether this observation would be reflected in the coefficients $C_{\alpha\beta}$ derived in the application of the inverse method. Indeed, for the numerical inverse method to be credible this observation must be reflected in the dominance of the relevant $3a'_1$ or $7a_q$ coefficient over those for the other orbitals of like symmetry.

4. Results and Discussion

We study first the results of our numerical inverse procedure investigation into the 2e' and 1e' orbitals of the highly-strained hydrocarbon cyclopropane. Von Niessen *et al.* (1994) had previously seen that their individual PWIA momentum distribution shapes were not well described by the appropriate Hartree–Fock (HF) orbital. This observation is reproduced in Figs 1*a* and 1*b* for the respective 2e' and 1e' orbitals, where the results using Hartree–Fock orbitals due to Snyder and Basch (1972) at the STO-14 level and GAMESS 92 (Schmidt *et al.* 1990) at the STO-36 level are given.

Considering Fig. 1*a*, it is immediately apparent that the present estimate of the normalised Dyson orbital, denoted as present orbital 1 (see Table 1 for the coefficients), provides a much better fit to the experimental 2e' MD data of von Niessen *et al.* (1994) than does that obtained using the basis 2e' orbital. This is well reflected by the value of χ^2 falling from 40, when the 2e' HF STO-36 orbital is employed, to a value of $1 \cdot 9$ with the orbital derived using the inverse procedure. As expected the basis 2e' orbital dominates in the expansion for the normalised Dyson orbital, the high-quality fit of Fig. 1*a* being achieved with only about a 2% core, 1e' and unoccupied orbital contribution (see Table 1).

A very similar story for the 1e' state is also found in Fig. 1b. In this case the present normalised Dyson orbital, again denoted as present orbital 1 (see Table 1 for its coefficients), compared to that obtained using the basis 1e' orbital, provides a far superior fit to the experimental 1e' MD data (see Fig. 1b). Here the value of χ^2 fell from 34, when the 1e' HF STO-36 orbital was employed, to a value of 11 with the derived normalised Dyson orbital. While it is clear from



Fig. 1. A comparison of PWIA calculations with experiment for (a) cyclopropane 2e' and (b) cyclopropane 1e'. The results using Hartree–Fock orbitals due to Snyder and Basch (1992) at the STO-14 level and GAMESS 92 (Schmidt *et al.* 1990) at the STO-36 level are given.



Fig. 2. A comparison of PWIA calculations with experiment for (a) cyclopropane 2e' and (b) cyclopropane 1e'. The additional-constrained normalised Dyson orbital is denoted as present orbital 2.

Table 1 that the basis 1e' orbital still dominates the expansion, to obtain the very good fit of Fig. 1b a 20% core, 2e' and unoccupied orbital contribution is now required. This higher contribution may be a reflection of our PWIA reaction mechanism description not being as exact for inner valence states as it is for outer valence states.

2e' orbital Present orbital 1		le' orbital Present orbital 1	
Core	-0.009 ± 0.199	Core	-0.203 ± 0.055
1e'	-0.127 ± 0.001	1e'	0.895 ± 0.002
2e'	0.990 ± 0.020	2e'	$0.388 {\pm} 0.045$
Unoccupied	$0.053 {\pm} 0.003$	Unoccupied	-0.080 ± 0.014

 Table 1. Fitting coefficients and their standard deviations for the 2e' and 1e' orbitals of cyclopropane

The experimental MDs of von Niessen *et al.* were placed on an absolute scale with a normalisation procedure fully described in that paper. Under these circumstances G = 1 and the scaling factor F^{α} reduces to the spectroscopic factor S_i^{α} , for that $i \ \epsilon \ \alpha$ as measured in the binding energy spectra in von Niessen *et al.* Recall the spectroscopic sum rule (equation 6) at this time. Application of the numerical inverse procedure to the 2e' MD at the binding energy (ε_f) 10·9 eV gave $S_{2e'} = 1.00\pm 0.03$, in good agreement with the result of the third-order algebraic diagrammatic construction ADC(3) calculation in von Niessen *et al.* (S = 0.91) and the Green function calculation (S = 0.95) of Cederbaum *et al.* (1978). Similarly, for the 1e' MD at $\varepsilon_f = 19.9$ eV we find $S_{1e'} = 0.85\pm 0.02$, again in good agreement with the available ADC(3) (S = 0.82) and Green function (S = 0.88) results.

 Table 2. Fitting coefficients and their standard deviations for the 2e' and 1e' orbitals of cyclopropane

In addition to the usual orthonormality constraint we have applied the restriction that χ^2 (equation 10) must be minimised for both Dyson orbitals simultaneously

2e' orbital Present orbital 2		le' orbital Present orbital 2	
Core	$0.116 {\pm} 0.067$	Core	0.017 ± 0.032
1e'	$-0.371 {\pm} 0.005$	1e'	$0.957 {\pm} 0.054$
2e'	0.921 ± 0.042	2e'	$0 \cdot 284 \pm 0 \cdot 010$
Unoccupied	$0.033 {\pm} 0.008$	Unoccupied	-0.054 ± 0.008

The 2e' and 1e' orbitals of cyclopropane are examples of orthonormal orbitals of like symmetry, but whose principal quantum numbers are different. As such we can not only constrain the fitting in the usual way by ensuring the orthonormality of the transformation matrix $C_{\beta\alpha}$ but, additionally, we can also require that the χ^2 fit to the respective 2e' and 1e' MDs, to derive the normalised Dyson orbitals, be minimised simultaneously. The results of this procedure are illustrated in Fig. 2a for the 2e' orbital and Fig. 2b for the 1e' orbital. In both cases the additional-constrained normalised Dyson orbital is denoted as present orbital 2. The fitting coefficients and their standard deviations for these normalised Dyson orbitals are given in Table 2. Note that the errors on the derived coefficients are generally small which reflects, at least in part, the statistical accuracy of the experimental MD data from von Niessen *et al.* and the well-defined nature of the experimental angular resolution.

The normalised Dyson orbitals (present orbitals 1 and 2 of Fig. 2a) derived using the usual and more constrained forms of the numerical inverse procedure, for the 2e' MD, are seen to be very similar (see also Tables 1 and 2 for the coefficients). This is, in addition, reflected in the similar χ^2 values for the fit using present orbital 1 (1·9) and present orbital 2 (5·1). Both lead to very good agreement with the experimental 2e' MD (see Fig. 2a) with the major difference between them being that the MD from present orbital 2 peaks at a slightly smaller value of ϕ (or p) compared to that for present orbital 1. For the 1e' MD (see Fig. 2b) the relevant derived normalised Dyson orbitals (again denoted as present orbitals 1 and 2) lead to MDs which are almost identical and which are both in excellent agreement with the experimental momentum distribution. Indeed the only major difference between them is that Present Orbital 2 gives a 1e' MD which is slightly larger in magnitude at the peak of the cross section



Fig. 3. A comparison of PWIA calculations with experiment for [1.1.1]propellane 3a'_1.

compared to the result obtained with present orbital 1. This point is further evidenced by the value of χ^2 obtained from the fit with present orbital 1 (~ 11) being only slightly smaller than that obtained with present orbital 2 (~ 15).

The similarity between the derived normalised Dyson orbitals, as determined from the usual (see Section 2) and more constrained inverse procedures and as reflected in their level of agreement with the experimental MDs for both the 2e' and 1e' states of cyclopropane, gives us further confidence in the underlying soundness of the technique. The normalised Dyson orbitals we obtain are not arbitrary artifacts of the fitting procedure we employ, the dominance of the relevant 2e' or 1e' basis orbital in each respective expansion being a further, clear, indication of this.

The numerical inverse procedures applied above, for both the usual (present orbital 1) and more constrained (present orbital 2) fitting cases, were also used in our study of the highest occupied molecular orbital $(3a'_1)$ of [1.1.1]propellane. Here the core, $1a'_1$, $2a'_1$, $3a'_1$ and $4a'_1$ (unoccupied) basis propellane orbitals were computed using GAMESS 92 with full details being found in Adcock *et al.* (1995). The results for the fitting coefficients and their standard deviations, for the normalised Dyson orbitals, can be found in Table 3 with the resultant $3a'_1$ MDs being illustrated in Fig. 3. Note that in this case the additional simultaneous χ^2 minimisation requirement is provided by the experimental $1a'_1$ MD data, although unlike our behaviour with cyclopropane these data are not specifically presented here.

In Fig. 3 it is apparent that the current estimates (present orbitals 1 and 2) of the normalised Dyson orbital provide a somewhat better fit to the experimental $3a'_1$ MD data of Adcock *et al.* (1997) than does that obtained using the basis $3a'_1$ orbital, a result consistent with what we found for cyclopropane. This point is also reinforced by the χ^2 values falling from $12 \cdot 7$ for the basis $3a'_1$ orbital to $8 \cdot 8$ when present orbital 2 is employed and $7 \cdot 8$ when present orbital 1 is used. There is a little difference between the resultant $3a'_1$ MDs from the two normalised Dyson orbitals, a point additionally reflected by their respective coefficients in Table 3. In both cases the coefficient for the $3a'_1$ basis orbital dominates. In the light of this result and those found earlier for cyclopropane, we will not apply the more constrained numerical inverse procedure to our analysis of 1,2-propadiene and trans 1,3-butadiene.

Table 3. Fitting coefficients and their standard deviations for the $3a'_1$ orbital of [1.1.1]propellane

Present orbital 1 refers to the normalised Dyson orbital determined with the usual orthonormality constraint (Section 2), while present orbital 2 denotes the derived normalised Dyson orbital so determined with the additional restriction provided by fitting the $1a'_1$ MD simultaneously and minimising both χ^2

$3a'_1$ orbital Present orbital 1		$3a'_1$ orbital Present orbital 2	
Orbital basis	Coefficient	Orbital basis	Coefficient
Core	$0.523 {\pm} 0.030$	Core	0.412 ± 0.047
$1a'_1$	$0 \cdot 180 {\pm} 0 \cdot 022$	$1a'_1$	0.051 ± 0.016
$2a'_1$	-0.239 ± 0.005	$2a'_1$	-0.129 ± 0.002
$3a'_1$	$0.794 {\pm} 0.019$	$3a'_1$	$0.898 {\pm} 0.021$
Unoccupied	-0.081 ± 0.013	Unoccupied	-0.058 ± 0.011

As the $3a'_1$ MD data, measured at $\varepsilon_f = 9.74$ eV, were already placed on an absolute scale by normalisation, in the manner described by Adcock *et al.* (1997), we note G = 1. Thus the derived scaling factor, which is identical for both present orbital 1 and present orbital 2, provides a direct measure of the spectroscopic factor for the $3a'_1$ orbital at that binding energy. We find $S_{3a'_1} = 0.88 \pm 0.03$, a value which is in excellent agreement (S = 0.89) with that calculated by Adcock *et al.* (1995) using an ADC(3) level formalism.



Fig. 4. A comparison of PWIA calculations with experiment for 1,2-propadiene 2e.

We next study the results of our numerical inverse procedure investigation into the 2e orbital of 1,2-propadiene. Braidwood *et al.* (1994) previously noted that its PWIA momentum distribution shape was not well described by a GAMESS calculated (Schmidt *et al.* 1990) Hartree–Fock orbital at the STO-36 level. This can clearly be seen in Fig. 4. Also shown in Fig. 4 is the present estimate of the normalised Dyson orbital, denoted as present orbital 1 (see Table 4 for coefficients), which provides a much better fit to the experimental 2e MD data of Braidwood *et al.* (1994) than does that obtained using the basis 2e orbital. This is well reflected by the value of χ^2 falling from 372, when the basis 2e HF STO-36 orbital is employed, to a value of 2·3 when the normalised is used. As expected the basis 2e orbital coefficient dominates the normalised Dyson orbital, the high-quality fit of Fig. 4 being achieved with only about a 6% 1e and unoccupied orbital contribution (see Table 4).

Table 4. Fitting coefficients and their standarddeviations for the 2e orbital of 1,2-propadiene			
2e orbital Present orbital 1	a		
Orbital basis	Coefficient		
le	0.085 ± 0.016		
2e Unoccupied	0.970 ± 0.001 0.229 ± 0.007		

The experimental 2e MD of Braidwood *et al.* was placed on an absolute scale with a normalisation technique fully described in that paper. Thus, similar to the circumstances for cyclopropane and [1.1.1]propellane, G = 1 and F^{α} reduces to the spectroscopic factor S_{i}^{2e} for the 2e orbital at the binding energy $\varepsilon_f = 10.25$ eV. The value of $S_{2e} = 0.89 \pm 0.02$ we found from the present analysis is in excellent agreement with the ADC(3) result of Braidwood *et al.* (S = 0.89) and in very good agreement with the Green function method calculation (S = 0.91) of Cederbaum *et al.* (1978). Note that the 1,2-propadiene wavefunction employed in the ADC(3) calculations (and the same is true for cyclopropane, [1.1.1]propellane and trans 1,3-butadiene) used the large atomic natural orbital (ANO) basis set of Widmark *et al.* (1990).

Finally we examine our results for the $7a_g$ orbital of trans 1,3-butadiene. For this molecule an extensive orthonormal basis consisting of the $1a_g$, $2a_g$, $3a_g$, $4a_g$, $5a_g$, $6a_g$, $7a_g$, $8a_g$ and $9a_g$ Hartree–Fock orbitals, all calculated with GAMESS



Fig. 5. A comparison of PWIA calculations with experiment for trans 1,3-butadiene $7a_q$.

92 at the STO-36 level, was employed. However, it soon became clear that the expansion coefficients $(C_{\beta\alpha})$ for the $2a_q$, $3a_q$, $4a_q$ and $5a_q$ basis orbitals were effectively 0 with their inclusion leading to no improvement to the value of χ^2 in the fit. Consequently they were omitted in the final fit. It is apparent from Fig. 5 that the determined normalised Dyson orbital leads to somewhat better agreement with the experimental $7a_g$ MD of Brunger *et al.* (1998) than that obtained with the $7a_q$ basis orbital alone. However, this improvement is not as clear cut here as it was before with the value of χ^2 only improving from about $1\cdot 3$ to 0.9. The main reason for this is that the uncertainties on the $7a_q$ experimental MD are larger than any of the other molecules we have considered. This is due to the 7a_q state being in close proximity (in terms of ε_f) to a couple of other orbitals whose MDs have much larger cross sections. Thus the deconvolution errors on it are significant (see Brunger et al. 1998). This effect is also evident in the uncertainties on the coefficients of the basis orbitals for the normalised Dyson orbital (see Table 5). Nonetheless the $7a_q$ basis orbital still dominates the expansion in the normalised Dyson orbital as one might intuitively expect.

Table 5. Fitting coefficients and their standarddeviations for the $7a_g$ orbital of trans 1,3-
butadiene

	$7a_a$ orbital	
	Present orbital 1	
Orbital basis		Coefficient
$1a_g$		0.270 ± 0.411
$6a_g$		0.044 ± 0.027
$7a_g$		0.918 ± 0.147
$8a_g$		-0.099 ± 0.082
$9a_g$		$0.269{\pm}0.035$

The independent normalisation by Brunger *et al.* (1998), of their 7a_g MD, again allows us to equate the derived scaling factor F^{α} directly with the spectroscopic factor S_i^{α} for this MD at the binding energy of its measurement ($\varepsilon_f = 12 \cdot 20 \text{ eV}$). The value determined in the present analysis, $S_{7a_g} = 0.79 \pm 0.12$, is consistent with the ADC(3) level calculations of both Michalewicz *et al.* (1997) (S = 0.89) and Holland *et al.* (1996) (S = 0.89).

5. Conclusions

We have applied our numerical inverse procedure to selected MDs of the organic molecules 1,2-propadiene, trans 1,3-butadiene, [1.1.1]propellane and cyclopropane. In each case the derived normalised Dyson orbital led to better agreement with the measured MD than did that for the basis orbital alone, although we note that the coefficient for this basis orbital dominated in the expansion, in each case considered, for the respective normalised Dyson orbitals. The spectroscopic factors determined in each application of the inverse procedure were also found to be in very good agreement with those calculated using ADC(3) and more general Green function approaches.

If we accept the proposition that the orbital wavefunction which best reproduces the experimental MD is the most physically reasonable representation for that orbital then it follows that this wavefunction, when combined with others that also make up the description of the molecule, should lead to more accurate molecular property information for the molecule in question. The interfacing of the output from our inverse technique program to UNICHEM (see Michalewicz *et al.* 1997), a supercomputer based suite of programs that enables calculation of molecular property information, is our next development so that we can test this hypothesis.

Acknowledgments

This paper is dedicated to Professor Erich Weigold to mark his 60th birthday on 19 October 1997. One of us (MJB) thanks the Australian Research Council for his Queen Elizabeth 2 Fellowship.

References

- Adcock, W., Brunger, M. J., Clark, C. I., McCarthy, I. E., Michalewicz, M. T., von Niessen, W., Weigold, E., and Winkler, D. A. (1997). J. Am. Chem. Soc. 119, 2896.
- Adcock, W., Brunger, M. J., Clark, C. I., McCarthy, I. E., Weigold, E., Michalewicz, M. T., Winkler, D. A., and von Niessen, W. (1995). *Chem. Phys. Lett.* 244, 433.
- Allen, L. J. (1986). Phys. Rev. A 34, 2706.
- Allen, L. J., and Burger, H. (1984). Phys. Rev. A 30, 1237.
- Allen, L. J., and McCarthy, I. E. (1987). Phys. Rev. A 36, 2570.
- Allen, L. J., Brunger, M. J., McCarthy, I. E., and Teubner, P. J. O. (1987). J. Phys. B 20, 4861.
- Andrick, D., and Bitsch, A. (1975). J. Phys. B 8, 393.
- Bevington, P. R., and Robinson, D. K. (1992). 'Data Reduction, and Error Analysis for the Physical Sciences' (McGraw–Hill: New York).
- Braidwood, S., Brunger, M. J., Konovalov, D. A., and Weigold, E. (1993). J. Phys. B 26, 1655.
- Braidwood, S., Brunger, M. J., Weigold, E., von Niessen, W., and Zakrzewski, V. G. (1994). J. Phys. B 27, 2075.
- Brion, C. E. (1992). Inst. Phys. Conf. Ser. 122, 171.
- Brunger, M. J., Buckman, S. J., Allen, L. J., McCarthy, I. E., and Ratnavelu, K. (1992). J. Phys. B 25, 1823.
- Brunger, M. J., Winkler, D. A., Michalewicz, M. T., and Weigold, E. (1998). J. Chem. Phys. 108, 1859.
- Buckman, S. J., Lun, A., Gibson, J. C., Allen, L. J., McEachran, R. P., and Parcell, L. A. (1998). J. Phys. B **31**, in press.
- Bürger, H., Allen, L. J., Fiedeldey, H., and Sofianos, S. A. (1983). Phys. Lett. A 97, 39.
- Cederbaum, L. S., Domcke, W., Schirmer, J., von Niessen, W., Diercksen, G. H. F., and Kraemar, W. P. (1978). J. Chem. Phys. 69, 1591.
- Chadan, K., and Sabatier, P. C. (1989). 'Inverse Problems in Quantum Scattering Theory', 2nd edn (Springer: New York).
- Duffy, P., Chong, D. P., Casida, M. E., and Salahub, D. R. (1994). Phys. Rev. A 50, 4707.
- Holland, D. M. P., MacDonald, M. A., Hayes, M. A., Baltzer, P., Wannberg, B., Lundqvist, M., Karlsson, L., and von Niessen, W. (1996). J. Phys. B 29, 3091.
- Leeb, H., Fiedeldey, H., and Lipperheide, R. (1985). Phys. Rev. C 32, 1223.

Lipperheide, R., and Fiedeldey, H. (1978). Z. Phys. A 286, 45.

- Lipperheide, R., and Fiedeldey, H. (1981). Z. Phys. A 301, 81.
- Lun, A., Chen, X.-J., Allen, L. J., and Amos, K. (1994). Phys. Rev. A 49, 3788.
- McCarthy, I. E., and Weigold, E. (1991). Rep. Prog. Phys. 54, 789.
- Michalewicz, M. T., Winkler, D. A., Brunger, M. J., McCarthy, I. E., and von Niessen, W. (1997). In 'Computational Chemistry, and Chemical Engineering' (Eds G. Cisneros et al.), pp. 280–90 (World Scientific: Singapore).
- Nicholson, R. J. F., McCarthy, I. E., and Weyrich, W. (1998). *Phys. Rev.* A, in preparation. Schmider, H., Smith, V. H., and Weyrich, W. (1990). *Trans. Amer. Cryst. Assoc.* 26, 125.

Schmider, H., Smith, V. H., and Weyrich, W. (1992). J. Chem. Phys. 96, 8986.

- Schmider, H., Smith, V. H., and Weyrich, W. (1993). Z. Naturforsch. 48a, 211.
- Schmidt, M. W., Baldridge, K. K., Boatz, J. A., Jensen, J. H., Koseki, S., Gordon, M. S., Nguyen, K. A., Windus, T. L., and Elbert, S. T. (1990). QCPE Bull. 10, 52. Snyder, L. C., and Basch, H. (1972). 'Molecular Wavefunctions, and Properties' (Wiley: New York).

von Niessen, W., Brunger, M. J., and Weigold, E. (1994). J. Phys. B 27, 4309.

Widmark, P. O., Malmquist, P.-A., and Roos, B. O. (1990). Theor. Chim. Acta 77, 291.

Manuscript received 25 September, accepted 4 December 1997