# The $^2B_1$ shape resonance in electron-formaldehyde scattering: an investigation using the dilated electron propagator method

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## Abstract

The zeroth order, second order, diagonal two particle one hole-Tamm Dancoff approximation and the corresponding quasi-particle decouplings of the dilated electron propagator have been applied to investigate the $^2B_1$ $HCHO^-$ shape resonance. The results from these calculations are in good agreement with the experimental and other theoretical results. The resonant orbital is shown to be the $> C = O$ $\pi^*$ orbital and the correlation and relaxation effects in conjunction with complex scaling assist resonance formation by lowering the antibonding nature of the $> C = O$ $\pi^*$ orbital to make it more suitable for metastable electron attachment.

## 1. Introduction

Resonances are known to arise from a pronounced change in electron scattering cross-section due to a temporary trapping of the impinging electron in one of the unoccupied orbitals of the target. These anions are short lived and decay by ejecting the electron into the continuum in times of $10^{-12}$ to $10^{-14}$ s in the gas phase [1]. Electron scattering off formaldehyde is of particular interest as it is the simplest molecule containing a highly polar carbonyl group, and a low-energy shape resonance corresponding to a quasibound $^2B_1$ state of $HCHO^-$ has been observed in elastic electron-formaldehyde collisions [2,3] as well as in vibrational excitation [4] at collision energies near 1 eV.

Ab initio calculations of the $^2B_1$ $HCHO^-$ attributes are few [5–7] with those using the complex Kohn variational method [6,7] providing the most reasonable description of this system. Due to the polarity of the carbonyl bond and the reorganisational effects accompanying the metastable electron attachment, strong correlation effects occur between the incident electron and the electrons of the target [6,7] and a need for a correlated treatment of the $HCHO^-$ attributes is highlighted by the unusually high value for the resonance energy calculated using the static exchange approximation [7]. Even after substantial incorporation of correlation effects, both the vibrational structure and the peak positions calculated using the complex Kohn variational method [7] differ from the experimental results, and the further investigation of this important prototypical resonance, involving a nonlinear polyatomic molecule, using other correlated techniques is of obvious importance.

The electron propagator theory [8–11] has emerged as a potent tool for the direct calculation of

the electron attachment energy, and when coupled with complex scaling [12,13] of all electronic coordinates, the resulting dilated electron propagator method [14–16] has emerged as an effective tool for the treatment of atomic and molecular shape resonances [17]. In this method, all the electronic coordinates in the Hamiltonian are scaled by a complex scale factor ($\eta = \alpha e^{i\theta}$) and the orbital energies and amplitudes are the zeroth-order poles and Feynman Dyson Amplitudes (FDAs) of the bi-orthogonal dilated electron propagator [17,18] which can be systematically improved using the second ($\Sigma^2$) and other higher order perturbative decouplings, or renormalised decouplings such as the diagonal two particle one hole-Tamm Dancoff Approximation (2ph-TDA) [8–11,19], to incorporate a greater extent of correlation and relaxation effects. The quasi-particle approximation [20–22] offers a more economic, yet reasonably accurate, computational approach.

A detailed study of these decouplings in the treatment of molecular resonances has established their effectiveness [17]. However, the applications so far have been on diatomic or linear nonpolar polyatomic molecules. It is therefore useful to employ the dilated electron propagator technique for calculating the shape resonance attributes of this prototypical nonlinear polar polyatomic system. The resonant poles of the dilated electron propagator furnish fairly accurate values for the resonance energy and the corresponding FDAs provide an orbital picture of resonance formation and decay. A study of $HCHO^-$ could therefore provide insights of general significance in designing feasible decouplings for the larger polyatomics.

Toward this end, it is our purpose in this Letter to present the main results obtained from an application of the zeroth order ($\Sigma^0$), the second order ($\Sigma^2$), the diagonal 2ph-TDA ($\Sigma^{2ph\text{-}TDA}$) and their quasi-particle variants the ($\Sigma_q^2$) and the ($\Sigma_q^{2ph\text{-}TDA}$) decouplings of the dilated electron propagator to the investigation of the $^2B_1$ $HCHO^-$ shape resonance, employing fairly balanced and systematically augmented basis sets.

The bi-orthogonal dilated electron propagator and its implementation have been discussed in detail elsewhere [17] and in the following section, we only offer the main formulae of immediate interest. The resonant poles and FDAs of HCHO are discussed in

Section 3 and a brief summary of the main results concludes this Letter.

## 2. Method

As in the case of the real, undilated one electron propagator [8–11], the bi-orthogonal dilated matrix electron propagator $\mathbf{G}(\eta, E)$ may also be expressed as [17]

$$\mathbf{G}^{-1}(\eta, E) = \mathbf{G}_0^{-1}(\eta, E) - \mathbf{\Sigma}(\eta, E) \tag{1}$$

where $\mathbf{G}_0(\eta, E)$ is the zeroth order propagator for the uncorrelated motion, here chosen as given by the bi-variational self-consistent field (SCF) approximation [23,24]. The self energy matrix $\mathbf{\Sigma}(\eta, E)$ contains the relaxation and correlation effects [17].

Solution of the bi-variational SCF equations [23,24] for the $N$-electron ground state yields a set of occupied and unoccupied orbitals. In terms of these spin orbitals, the matrix elements of $\mathbf{G}_0^{-1}(\eta, E)_{ij}$ are

$$\left(\mathbf{G}_0^{-1}(\eta, E)\right)_{ij} = (E - \epsilon_i)\,\delta_{ij} \tag{2}$$

where $\epsilon_i$ is the orbital energy corresponding to the $i$-th spin orbital. Through the second order in electron interaction, the elements of the self-energy matrix are

$$\Sigma_{ij}^2(\eta, E) = \frac{1}{2} \sum_{k,\ell,m} N_{k,\ell,m} \frac{\langle ik \| lm \rangle \langle lm \| jk \rangle}{(E + \epsilon_k - \epsilon_l - \epsilon_m)}, \tag{3}$$

where

$$N_{klm} = \langle n_k \rangle - \langle n_k \rangle \langle n_l \rangle - \langle n_k \rangle \langle n_m \rangle$$
$$+ \langle n_l \rangle \langle n_m \rangle \tag{4}$$

with $\langle n_k \rangle$ being the occupation number for the $k$-th spin orbital and the antisymmetric two-electron integral

$$\langle ij \| k\ell \rangle = \eta^{-1} \int \psi_i(1)\psi_j(2)\left[(1 - P_{12})/r_{12}\right]$$
$$\times \psi_k(1)\psi_l(2)\,\mathrm{d}x_1\,\mathrm{d}x_2 \tag{5}$$

where the lack of complex conjugation stems from the bi-orthogonal set of orbitals resulting from bi-

variational SCF being the complex conjugate of each other [23]. For the diagonal 2ph-TDA decoupling of the dilated electron propagator

$$\Sigma_{ij}^{\text{2ph-TDA}}(\eta,E) = \frac{1}{2} \sum_{k,\ell,m} N_{k,\ell,m}$$

$$\times \frac{\langle ik \| \ell m \rangle \langle \ell m \| jk \rangle}{(E + \epsilon_k - \epsilon_l - \epsilon_m - \Delta)}, \quad (6)$$

where

$$\Delta = \frac{1}{2}\langle m\ell \| m\ell \rangle (1 - \langle n_m \rangle - \langle n_l \rangle) - \langle km \| km \rangle$$

$$\times (\langle n_k \rangle - \langle n_m \rangle) - \langle k\ell \| k\ell \rangle (\langle n_k \rangle - \langle n_l \rangle). \quad (7)$$

The usual dilated electron propagator calculations proceed by iterative solutions of the eigenvalue problem

$$\mathbf{L}(\eta,E)\chi_i(\eta,E) = \mathscr{E}_i(\eta,E)\chi_i(\eta,E) \quad (8)$$

with

$$\mathbf{L}(\eta,E) = \boldsymbol{\epsilon} + \boldsymbol{\Sigma}(\eta,E) \quad (9)$$

where $\boldsymbol{\epsilon}$ is the diagonal matrix of orbital energies and $\boldsymbol{\Sigma}$ is the self energy matrix. The propagator pole $\mathscr{E}_i(\eta,E)$ is obtained by iterative diagonalisation such that one of the eigenvalues $\mathscr{E}_i(\eta,E)$ fulfills the condition $\mathscr{E}_i(\eta,E) = E$. Conform the complex scaling theorems [12,13], the poles which display stability with respect to variations in the complex scaling parameter are associated with resonances. The real part of the resonant pole furnishes the e nergy and the imaginary part the half width of the resonance.

The quasi-particle approximation for the dilated electron propagator [22] results from a diagonal approximation to the self-energy matrix $\boldsymbol{\Sigma}(\eta,E)$ with poles of the dilated electron propagator given by

$$\mathscr{E}_i(\eta,E) = \epsilon_i + \Sigma_{ii}(\eta,E) \quad (10)$$

which are determined iteratively beginning with $E = \epsilon_i$ and $\Sigma_{ii}$ may correspond to any perturbative ($\Sigma^2$) or renormalised decoupling such as the diagonal 2ph-TDA ($\Sigma^{\text{2ph-TDA}}$).

In the bi-variationally obtained bi-orthogonal orbital basis $\{\psi_i\}$, $\chi_n$ is a linear combination

$$\chi_n(\boldsymbol{r}) = \sum_i C_{ni}\psi_i(\boldsymbol{r}) \quad (11)$$

where the mixing of the canonical orbitals allows for the incorporation of correlation and relaxation effects. In the zeroth ($\boldsymbol{\Sigma} = \mathbf{0}$) and quasiparticle approximations (diagonal $\boldsymbol{\Sigma}$), there is no mixing. The difference between the perturbative second order ($\Sigma^2$) or renormalised diagonal 2ph-TDA ($\Sigma^{\text{2ph-TDA}}$) decouplings manifests itself through the differences between the mixing coefficients $C_{ni}$ from these approximations.

## 3. Results and discussion

The Gaussian basis sets employed in our calculations utilize the 4s,2p contracted Gaussian type orbitals (CGTOs) for carbon and oxygen and 2s CGTOs for hydrogen from Dunning's compilation [25]. This basis was augmented with four additional p-type and one d-type function $\{\alpha(\text{p}) = 0.0382, 0.01232, 0.004107, 0.001325; \ \alpha(\text{d}) = 0.0653\}$ on carbon, $\{\alpha(\text{p} = 0.0689, 0.0222, 0.00717, 0.000746; \ \alpha(\text{d}) = 1.211\}$ on oxygen and one p-type function $\{\alpha(\text{p}) = 0.07\}$ on hydrogen atoms to obtain the 66 CGTO basis (I) with 4s,6p,1d CGTOs on C and O and 2s,1p CGTOs on H atoms. Resonant theta trajectories from this 66 CGTO basis for all decouplings are plotted in Fig. 1a–d. The 66 CGTO basis was further augmented by adding extra p functions, one at a time, on carbon, oxygen, and hydrogen atoms by scaling the lowest p exponent by 0.25. The basis sets so obtained were 4s6p1d on C/4s7p1d on O/2s1p on H (II); 4s7p1d on C/4s6p1d on O/2s1p on H (III); 4s7p1d on C/4s7p1d on O/2s1p on H (IV); 4s8p1d on C/4s8p1d on O/2s1p on H (V) and finally the 4s8p1d on C/4s8p1d on O/2s2p on H (VI) with an extra p function on H as well. The resonant theta trajectories from all the bases for the $\Sigma^2$ decoupling are plotted in Figs. 1d–i.

The resonance energy and width for the $^2\text{B}_1$ HCHO$^-$ shape resonance obtained from the quasi-stable portion of theta-trajectories from the bases catalogued above, along with those from other theo-

( )
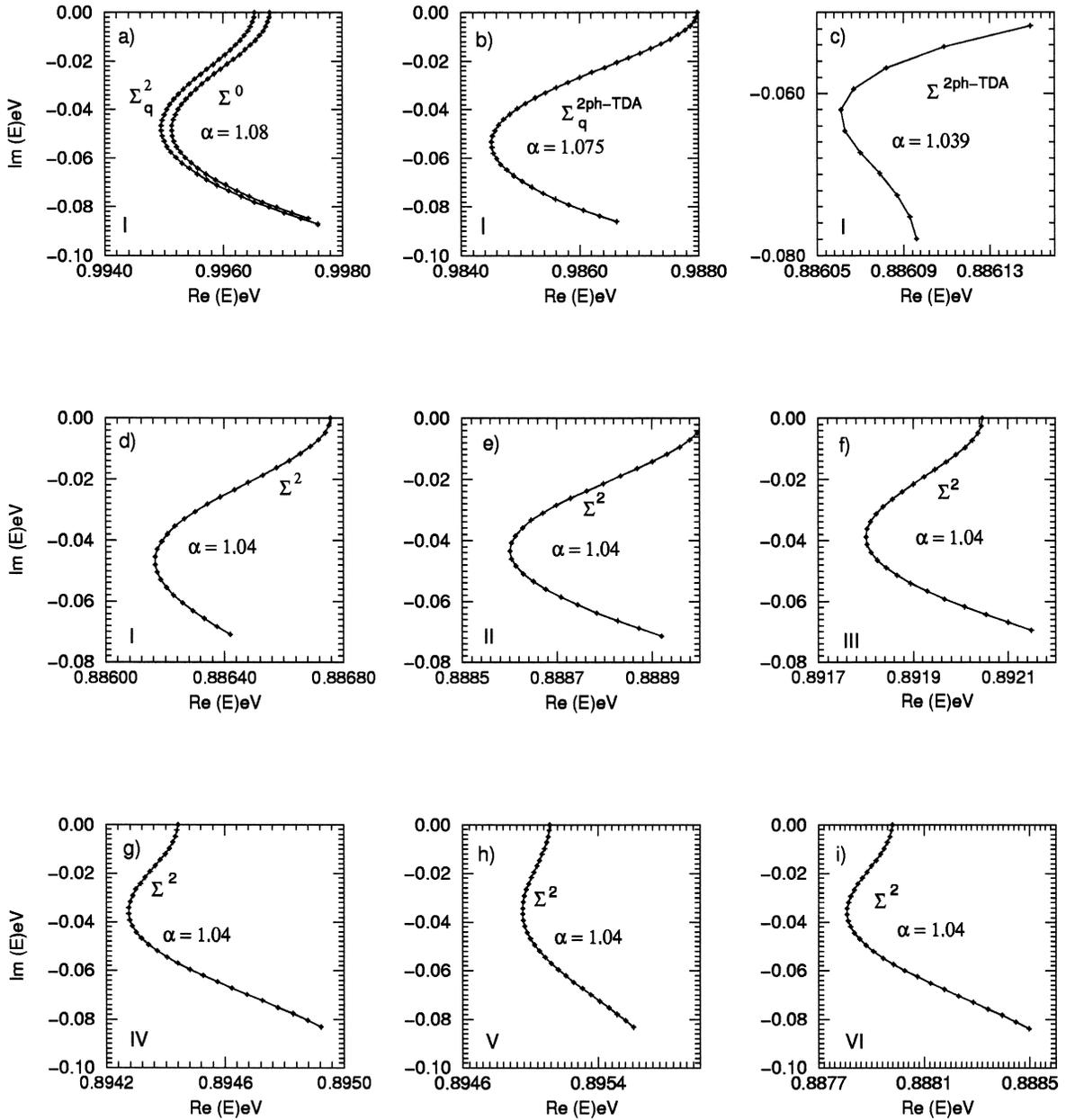


Fig. 1. Theta trajectories from different decouplings of the dilated electron propagator using basis I (a–d) and from second order decoupling using the bases I–VI (d–i). The trajectories start on the real line ($\theta = 0.0$) and $\theta$ increments are in steps ($\theta_{\text{inc}}$) of 0.001 radians.

retical and experimental methods, are collected in Table 1. The large discrepany of 2 eV between the Static Exchange (SE) and Complex Kohn results of Schneider et al. [7] has been attributed by them to the lack of target distortion in the SE approximation.

The results of Kurtz and Jordan [26] for the $^2P$ and $^2D$ shape resonances in e–Be, e–Mg and e–Ca scattering display similar behaviour and the SE results are many times larger than those where target polarisation has been included. In case of the $^2B_1$

Table 1
Energy and width of the $^2B_1$ HCHO$^-$ shape resonance

| Method/reference | Energy (eV) | Width (eV) |
|---|---|---|
| *Experiment*: | | |
| Electron transmission [2,3] | 1.0/0.86 | |
| Vibrational excitation [4] | 0.87 | |
| *Theoretical treatments*: | | |
| Static exchange [6] | 3.0 | |
| Complex Kohn [7] | 1.0 | 0.5 |
| *Dilated electron propagator* (this work) | | |
| Zeroth order | 1.0 | 0.10 |
| Quasiparticle second order | 0.99 | 0.10 |
| Quasiparticle diagonal 2ph-TDA | 0.98 | 0.11 |
| Diagonal 2ph-TDA | 0.89 | 0.12 |
| Second order {I/II/III/IV/V/VI} | 0.886/0.888/0.891 | 0.09/0.086/0.077 |
| | 0.894/0.895/0.887 | 0.073/0.073/0.076 |

I (4s6p1d on C/4s6p1d on O/2s1p on H). II (4s6p1d on C/4s7p1d on O/2s1p on H). III (4s7p1d on C/4s6p1d on O/2s1p on H).
IV (4s7p1d on C/4s7p1d on O/2s1p on H). V (4s8p1d on C/4s8p1d on O/2s1p on H). VI (4s8p1d on C/4s8p1d on O/2s2p on H).

HCHO$^-$, the polarity of the $>C=O$ group means that long range polarisation will be important and that care should be taken to include a sufficiently large number of diffuse p-type functions and additional d-type functions to accomodate polarisation effects. This has been attempted systematically and the resonance energy from different bases and decouplings of the bi-orthogonal dilated electron propagator compare favourably with those obtained from experiments [2–4] and other more accurate theoretical methods [7]. The widths from our dilated electron propagator calculations are, however much, narrower.

The resonance energies obtained using the $\Sigma^2$ decoupling from both basis II and basis III are extremely close to each other and when compared with those from basis I show that the CGTO basis on both the O and the C atoms are separately balanced and nearly saturated. Results from the 66 CGTO basis (I) and the largest 84 CGTO basis (VI) differ only marginally and further saturation of basis sets was therefore not attempted. The near saturation of basis set effects can be easily seen from the values from different bases collected in Table 1. The difference between $\Sigma^2$ results from bases VI and I is much smaller than the basis I results using different decouplings. We may therefore infer that the correlation and relaxation effects incorporated by the $\Sigma^2$ decoupling are more important than the basis set

effects and the basis sets employed are nearly saturated.

As discussed earlier, the resonant poles of the dilated electron propagator furnish the energy and the width; and the corresponding FDAs serve as the correlated orbitals involved in the metastable electron attachment [17]. An examination of the resonant FDAs can, therefore, provide useful insights. The resonant FDA on the real line using basis I and the $\Sigma^2$ decoupling is displayed in Fig. 2a. That the resonant FDA is indeed the $>C=O$ $\pi^*$ orbital as expected is brought out by the plot of the resonant FDA on both the real line ($\theta = 0.0$) and for the optimal value of $\theta$ ($\theta_{opt} = 0.02$ radians) in Figs. 2a–2c. The complete lack of amplitude on the H atoms and the presence of a large amplitude on carbon, as opposed to the oxygen, leaves little doubt that the electron attachment takes place in a localized $>C=O$ $\pi^*$ orbital and thus it can be seen that the dilated electron propagat or furnishes an effective tool for eliciting mechanistic details of the formation and decay of resonances.

It can also be seen from Fig. 2c that although the imaginary part of the resonant FDA is in general much smaller than the real part (Fig. 2b), complex scaling plays an important role in resonance stabilisation by redistributing the electron amplitude towards the more electronegative O atom. The difference between the probability density from FDAs at

Second order FDA (θ = 0.0)

Second order FDA (θ = θ_opt)



a)



b)
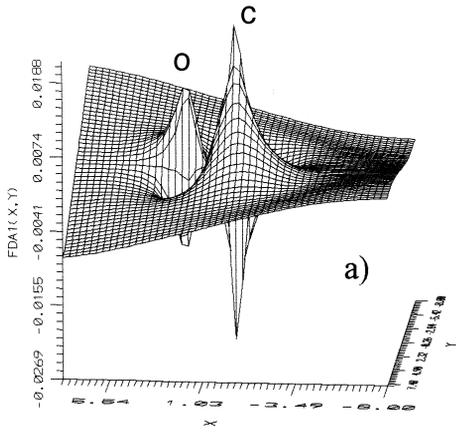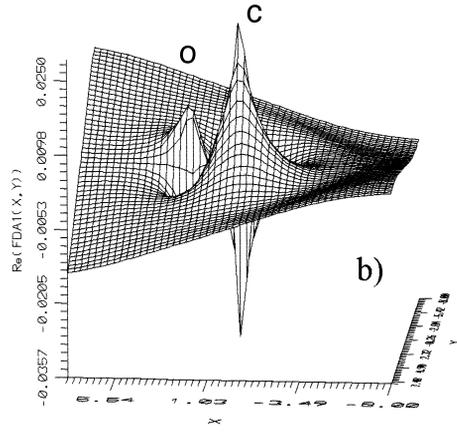
Second order FDA  (θ = θ_opt)

Probability density difference



c)



d)
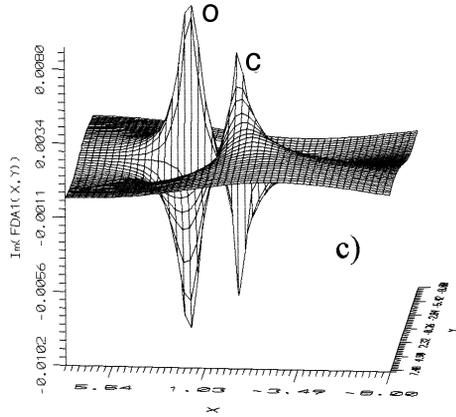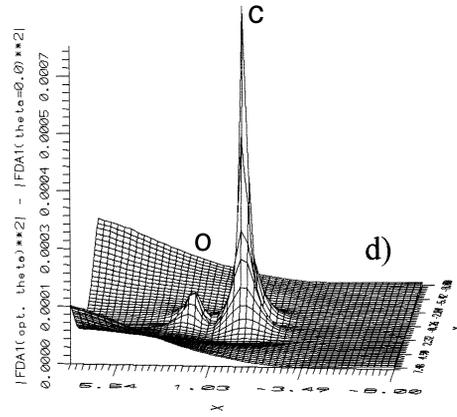
Amplitude difference  (θ = 0.0)

Amplitude difference  (θ = 0.0)



(e)



(f)
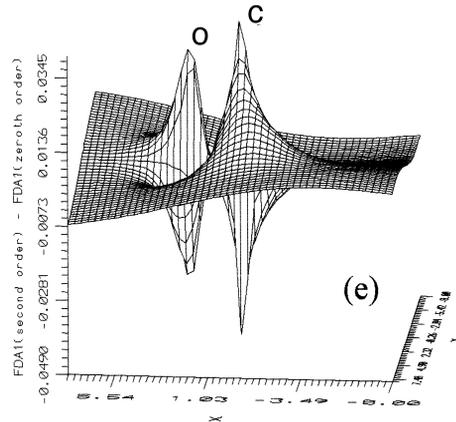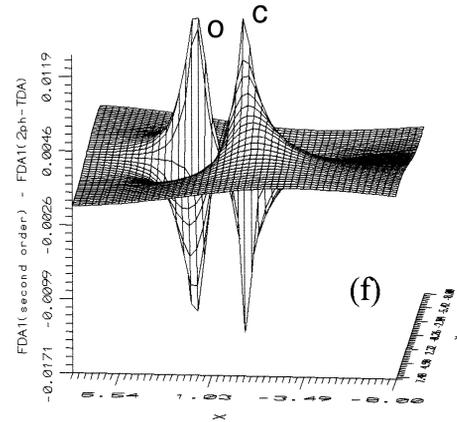
$\theta = 0.0$ and $\theta = \theta_{opt} = 0.02$ radians (Figs. 2a–2c) is plotted in Fig. 2d. The magnitude of probability density differences are small and although the primary role of complex scaling seems to be in identifying the resonant pole, it also provides some extra accumulation of electron density around both the carbon and the oxygen atoms which should stabilise electron attachment.

As can be seen from Table 1, the resonance energy and width from decouplings permitting orbital relaxation ($\Sigma^2$ and $\Sigma^{2ph\text{-}TDA}$) are similar and lower compared to those from the decouplings devoid of orbital mixing ($\Sigma^0, \Sigma_q^2$ and $\Sigma_q^{2ph\text{-}TDA}$), differing by as much as 0.1 eV for the resonance energy. This indicates that orbital relaxation has an important role in resonance formation and the lowering of widths in the $\Sigma^2$ and $\Sigma^{2ph\text{-}TDA}$ decouplings shows that correlation/relaxation effects stabilize the resonance. These features are amply brought out by the difference in basis I FDAs from different decouplings plotted in Figs. 2e and 2f. It can be seen that the difference between $\Sigma^2$ and $\Sigma^0$ FDAs (Fig. 2e) is much larger than that between $\Sigma^2$ and $\Sigma^{2ph\text{-}TDA}$ FDAs (Fig. 2f) and compared to both $\Sigma^0$ and $\Sigma^{2ph\text{-}TDA}$, the $\Sigma^2$ decoupling builds extra amplitude both on C and O atoms thereby reducing the antibonding nature of this FDA to assist in resonant electron attachment.

## 4. Concluding remarks

Our investigation of the $^2B_1$ shape resonance in the electron-formaldehyde scattering using the dilated electron propagator method has led to confirmation of the $>C=O$ $\pi^*$ orbital of formaldehyde as the resonant orbital. The unoccupied orbitals are extremely susceptible to basis set variations and the consistency in the resonance energies and widths, and also the orbital topology from different decouplings and bases, inspires confidence in the effectiveness of the dilated electron propagator technique in the characterization of resonance attributes. The results from the different decouplings employed to investigate the correlation and relaxation effects in the formation of $HCHO^-$ shape resonance show that the second order ($\Sigma^2$) decoupling leads to the largest accumulation of orbital amplitude in the carbon-oxygen region. The computationally more demanding diagonal 2ph-TDA, which sums the diagonal ring and ladder diagrams to all orders [8,27] did not provide any improvement.

A comparison between the results from the single orbital bi-variational SCF ($\Sigma^0$) and quasi-particle decouplings ($\Sigma_q^2$ and $\Sigma_q^{2ph\text{-}TDA}$), with those from $\Sigma^2$ and $\Sigma^{2ph\text{-}TDA}$ decouplings permitting the mixing of orbitals, shows that orbital relaxation plays an important role in molecular resonance formation. Complex scaling is seen to provide additional electron density on the C and O atoms, facilitating electron attachment. A comparison of results from different bases indicates that basis sets are nearly saturated and the basis set effects are smaller in comparison to the correlation and relaxation effects incorporated by higher order decouplings.

The calculated energies are in fairly good agreement with those from experiment and other accurate theoretical methods. The calculated widths are, however, much narrower. The widths calculated for other molecular resonances using the dilated electron propagator technique have been similarly narrow [17] and this seems to indicate an insufficiency of interelectronic repulsion. The incorporation of higher order decouplings, such as the third and the partial-fourth order, is an obvious extension for the provision of a more accurate description of resonances. Electron attachment in an anti-bonding orbital is known to result in the widths becoming narrower with the stretching of the bond involved in the resonance formation. In our calculation, a stretch of the $C=O$ bond by 0.1 a.u. leads to the width becoming 0.04 eV and because of this rapid decrease in width, we have not attempted an investigation of the effect of bond stretching on the resonance attributes. A treat-

Fig. 2. Feynman Dyson Amplitude (FDA) from the second order decoupling using basis (I) for $\alpha = 1.04$ at $\theta = 0.0$ (a); the real (b) and imaginary part (c) for $\theta = \theta_{opt} = 0.02$ radians and (d) the difference between probability densities from the $\Sigma^2$ FDA at $\theta = \theta_{opt}$ and $\theta = 0.0$. The difference between basis I FDAs at $\alpha = 1.04$ and $\theta = 0.0$ from (e) the second and the zeroth order decouplings and (f) the second and the diagonal 2ph-TDA decouplings.

ment including the third and the partial-fourth order decouplings and bond stretching would be of obvious importance and is the proposed focus of our future work.

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