Proc. Indian Acad. Sci. (Chem. Sci.), Vol. 106, No. 2, April 1994, pp. 111–121.

Treatment of $Be^+(1s^{-1})^2S$ Auger resonance with different decouplings of the dilated electron propagator

MILAN N MEDIKERI and MANOJ K MISHRA*
Department of Chemistry, Indian Institute of Technology, Powai, Bombay 400076, India

Abstract. The diagonal 2ph-TDA and quasiparticle decouplings of the dilated electron propagator (based on an underlying bi-variational SCF) are utilized to calculate energy and width of the $Be^+(1s^{-1})^2S$ Auger resonance for the first time. Comparison with experimental and other theoretical results reveals that the renormalized infinite order diagonal 2ph-TDA decoupling seems to offer a less balanced approach to the treatment of resonances than the second-order decoupling. The diagonal quasiparticle approximation to the self energy is seen to offer an effective and economic alternative to the non-diagonal propagator calculations.

Keywords. Auger resonance; dilated electron propagator; decoupling.

1. Introduction

The electron propagator theory (Linderberg and Öhrn 1973; Jörgensen and Simons 1981) has provided an effective route to the calculation of electron detachment (Cederbaum and Domcke 1977; Herman *et al* 1981; Öhrn and Born 1981; von Niessen *et al* 1984) and attachment (Simons 1977, 1978) energies and is well established as a powerful tool for the correlated treatment of electronic structure (Ortiz 1992) and dynamics (Meyer 1989; Cederbaum 1990; Meyer *et al* 1992). The dilated electron propagator (Mishra 1989) where electronic co-ordinates have been scaled by a complex scaling (Junker 1982; Reinhardt 1982; Ho 1983) factor ($\eta = \alpha e^{i\theta}$) has emerged as a convenient method for the direct calculation of energies and widths of shape resonances in electron–atom (Winkler 1979; Donnelly and Simons 1980; Mishra *et al* 1981a, 1983; Winkler *et al* 1981; Donnelly 1982a; Medikeri *et al* 1993) and electron–molecule scattering (Donnelly 1982b, 1985, 1986).

The spectral representation of the matrix-dilated electron propagator,

$$G_{sr}(\eta, E) = \lim_{\varepsilon \to 0^+} \sum_s \left[\frac{\langle \Psi_0^N | a_s | \Psi_s^{N+1} \rangle \langle \Psi_s^{N+1} | a_r^\dagger | \Psi_0^N \rangle}{E - (E_s^{N+1}(\eta) - E_0^N) + i\varepsilon} + \frac{\langle \Psi_0^N | a_r^\dagger | \Psi_s^{N-1} \rangle \langle \Psi_s^{N-1} | a_s | \Psi_0^N \rangle}{E - (E_0^N - E_s^{N-1}(\eta)) - i\varepsilon} \right], \tag{1}$$

provides for the simultaneous calculation of both the energy (real part) and width (twice the imaginary part) of electron detachment Auger ($E_0^N - E_s^{N-1}(\eta)$) and electron attachment shape resonances ($E_s^{N+1}(\eta) - E_0^N$) from its appropriate poles. The pole structure of the dilated electron propagator has been discussed in detail elsewhere

*For correspondence

(Donnelly and Simons 1980; Mishra *et al* 1983c) but it is obvious from (1) that since resonant eigenvalues ($E_r - i(\Gamma/2)$) have a negative imaginary part to account for their finite life time (Das and Melissinos 1986; Mishra 1994) and the target ground state energy E_0^N is completely real, the poles corresponding to the Auger resonances will have a positive imaginary part and their trajectory as a function of variations in the scaling parameter α or θ will move in the first quadrant of the complex energy plane. The complex poles in the first quadrant displaying quasi-stability with respect to variations in η are associated with Auger resonances (Palmquist *et al* 1981; Mishra *et al* 1983c).

These complex poles are searched through an iterative diagonalization procedure (Donnelly and Simons 1980), necessitating multiple passes through large self energy lists (von Niessen *et al* 1984) and the quest for quasi-stability of the resonant poles necessitates the construction of the dilated electron propagator for a large number of η values with 4–6 α and approximately 30 θ values per α being fairly representative. These two features, coupled with non-hermiticity and the complex (as opposed to real) nature of the underlying arithmetic makes the dilated electron propagator calculations approximately 100 times more demanding than their real counterparts. Exploration of effective and economic decouplings like the quasiparticle approximation (Holneicher *et al* 1972; Kurtz and Öhrn 1978; Ortiz and Öhrn 1980; von Niessen *et al* 1984; Ortiz 1990; Medikeri and Mishra 1993) is therefore an acute necessity for the dilated electron propagator calculations.

Furthermore, the meta-stable nature of resonances affords considerable interaction between the target and the decaying electron and reliable treatment of resonances calls for the incorporation of higher order or renormalized decouplings in the construction of the dilated electron propagator. A popular approximation for achieving this end has been the diagonal 2ph-TDA decoupling. Considerable experience with the real propagator calculations has shown that the diagonal and full 2ph-TDA decouplings being infinite order renormalized summation of the most important ring and ladder diagrams, offer enhanced level of correlation in the treatment of ionization energies and electron affinities (Cederbaum and Domcke 1977; Öhrn and Born 1981; von Niessen *et al* 1984).

To attend to these concerns and afford greater correlation with effective economy in the treatment of resonances, we have recently grafted the diagonal 2ph-TDA (Medikeri *et al* 1993, 1994), quasiparticle diagonal 2ph-TDA and quasiparticle second-order decouplings (Medikeri and Mishra 1993b) on to the dilated electron propagator technique as well. The effectiveness of these new decouplings of the dilated electron propagator has, however, been explored only through their employment in the treatment of electron attachment shape resonances. In fact, except for a few exceptions (Palmquist *et al* 1981; Mishra *et al* 1983c) almost all applications of the dilated electron propagator, including our own, have focused almost exclusively on the treatment of shape resonances.

Application of the diagonal 2ph-TDA and quasiparticle decouplings to the treatment of electron detachment ($1s^{-1}$) Auger resonance in Be^+ offers a complementary test for the effectiveness of these decouplings and is the principal concern of this paper.

The bi-orthogonal dilated electron propagator and its implementation has been discussed in detail elsewhere (Mishra *et al* 1981a; Medikeri *et al* 1993) and in the following section we offer only a skeletal outline of equations and the computational strategy of immediate relevance to this work. A brief discussion of our results concludes this paper.

2. Method

The Dyson equation for the bi-orthogonal matrix electron propagator $\mathbf{G}(\eta, E)$ may be expressed as (Mishra *et al* 1981a)

$$\mathbf{G}^{-1}(\eta, E) = \mathbf{G}_0^{-1}(\eta, E) - \boldsymbol{\Sigma}(\eta, E), \tag{2}$$

where $\mathbf{G}_0(\eta, E)$ is the zeroth order propagator for the uncorrelated electron motion, here chosen as given by the bi-variational SCF approximation (Mishra *et al* 1981b; Froelich and Löwdin 1983; Löwdin *et al* 1989). The self-energy matrix $\boldsymbol{\Sigma}(\eta, E)$ contains the relaxation and correlation effects.

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

$$(\mathbf{G}_0^{-1}(\eta, E))_{ij} = (E - \varepsilon_i)\delta_{ij}, \tag{3}$$

where ε_i is the orbital energy corresponding to spin orbital i. Through the second order of electron interaction, the elements of the self-energy matrix are

$$\sum_{ij}^{2}(\eta, E) = \frac{1}{2}\sum_{k,l,m} N_{klm}\frac{\langle ik \| lm\rangle\langle lm \| jk\rangle}{(E + \varepsilon_k - \varepsilon_l - \varepsilon_m)}, \tag{4}$$

where

$$N_{klm} = \langle n_k\rangle - \langle n_k\rangle\langle n_l\rangle - \langle n_k\rangle\langle n_m\rangle + \langle n_l\rangle\langle n_m\rangle, \tag{5}$$

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

$$\langle ij \| kl\rangle = \eta \int \psi_i(1)\psi_j(2)[(1 - P_{12})/r_{12}] \times \psi_k(1)\psi_l(2)\mathrm{d}x_1\,\mathrm{d}x_2. \tag{6}$$

The lack of complex conjugation stems from the bi-orthogonal set of orbitals resulting from bi-variational SCF being complex conjugate of each other (Mishra *et al* 1981b). For the diagonal 2ph-TDA (Cederbaum and Domcke 1977; Öhrn and Born 1981; von Niessen *et al* 1984) decoupling of the dilated electron propagator (Medikeri *et al* 1993)

$$\sum_{ij}^{\text{2ph-TDA}}(\eta, E) = \frac{1}{2}\sum_{k,l,m} N_{klm}\frac{\langle ik \| lm\rangle\langle lm \| jk\rangle}{(E + \varepsilon_k - \varepsilon_l - \varepsilon_m) - \Delta}, \tag{7}$$

where

$$\Delta = \frac{1}{2}\langle ml \| ml\rangle(1 - \langle n_m\rangle - \langle n_l\rangle) - \langle km \| km\rangle(\langle n_k\rangle - \langle n_m\rangle) - \langle kl \| kl\rangle(\langle n_k\rangle - \langle n_l\rangle). \tag{8}$$

The usual dilated electron propagator calculation proceeds by iterative diagonalization of

$$\mathbf{L}(\eta, E) = \varepsilon + \boldsymbol{\Sigma}(\eta, E). \tag{9}$$

with propagator pole E being a complex value such that one of the eigenvalues

$\{\varepsilon_n(\eta, E)\}$ of $\mathbf{L}(\eta, E)$ fulfills the condition $E = \varepsilon_n(\eta, E)$ (Donnelly and Simons 1980). The quasiparticle approximation for dilated electron propagator results from a diagonal approximation to the self-energy matrix $\Sigma(\eta, \mathbf{E})$ with poles of the dilated electron propagator being given by

$$E(\eta) = \varepsilon_i + \Sigma_{ii}(\eta, E), \tag{10}$$

which is solved iteratively beginning with $E = \varepsilon_i$ and Σ_{ii} may correspond to any perturbative or renormalized decoupling (Medikeri and Mishra 1993).

3. Results and discussion

Results from our calculations using various decouplings of the dilated electron propagator discussed earlier are portrayed in figures 1 and 2. The marked disparity between the theta trajectories for the uncorrelated SCF and propagator poles makes apparent the magnitude of correlation and relaxation effects attending the Auger resonance formation. From figure 2 it is seen that the diagonal 2ph-TDA approximation predicts higher energy and smaller width (longer lifetime) for the $Be^+(1s^{-1})^2S$ Auger resonance. The choice of basis set and the optimal α value (0·85) are those from an earlier study (Mishra *et al* 1983c). The theta trajectories for the quasiparticle diagonal 2ph-TDA for this optimal alpha shows multiple inflection points and cusps and therefore we have plotted theta trajectories for other nearby alpha values in figure 3. Because of multiple regions of quasi-stability in many of these trajectories, the quasi-stable value of the Auger pole for this decoupling has been elicited from the alpha trajectory for $\theta = 0{\cdot}17$ radians, the angle for which there is a clear stability in the only regular trajectory ($\alpha = 0{\cdot}75$) from this decoupling. The theta trajectories for other α values also display some stability for this $\theta_{opt} = 0{\cdot}17$ radians, in the sense of much more rapid decrease in ΔE as a function of the same uniform $\Delta\theta$ stepwise (i.e. numerical stability at least to first order). This alpha trajectory for the quasi-particle 2ph-TDA decoupling is displayed in figure 4. The distances narrow as we approach $\alpha = 0{\cdot}85$ and then increase again. This quasi-stable value in the alpha trajectory has been taken the best estimate of the resonant Auger pole form this decoupling.

The values for the energies and widths of the $Be^+(1s^{-1})^2S$ Auger resonance from these calculations along with experimental and other theoretical results are collected in table 1. It is clear from the figures and table 1 that, results from both the diagonal 2ph-TDA and quasiparticle diagonal 2ph-TDA seem to move away from the second order results towards those from the uncorrelated zeroth order bi-variational SCF calculations. Instead of being an improvement on the second order results, they deviate even more from the experimental (Bisgard *et al* 1978; Rodbro *et al* 1979) and other more reliable theoretical calculations (Kelly 1974). This behaviour of the diagonal 2ph-TDA where they offer little or no improvement on the second-order results has also been observed in our shape resonance calculations (Medikeri *et al* 1993a, c). We hasten to mention that Auger decay is a correlated event and its description at the SCF level is not meaningful. We have included the energy and widths from bi-variational SCF, only to assist in assessing the role of correlation and relaxation in the characterization of the Auger resonances as also to highlight the relatively poor quality of diagonal and quasiparticle diagonal 2ph-TDA results for this case.

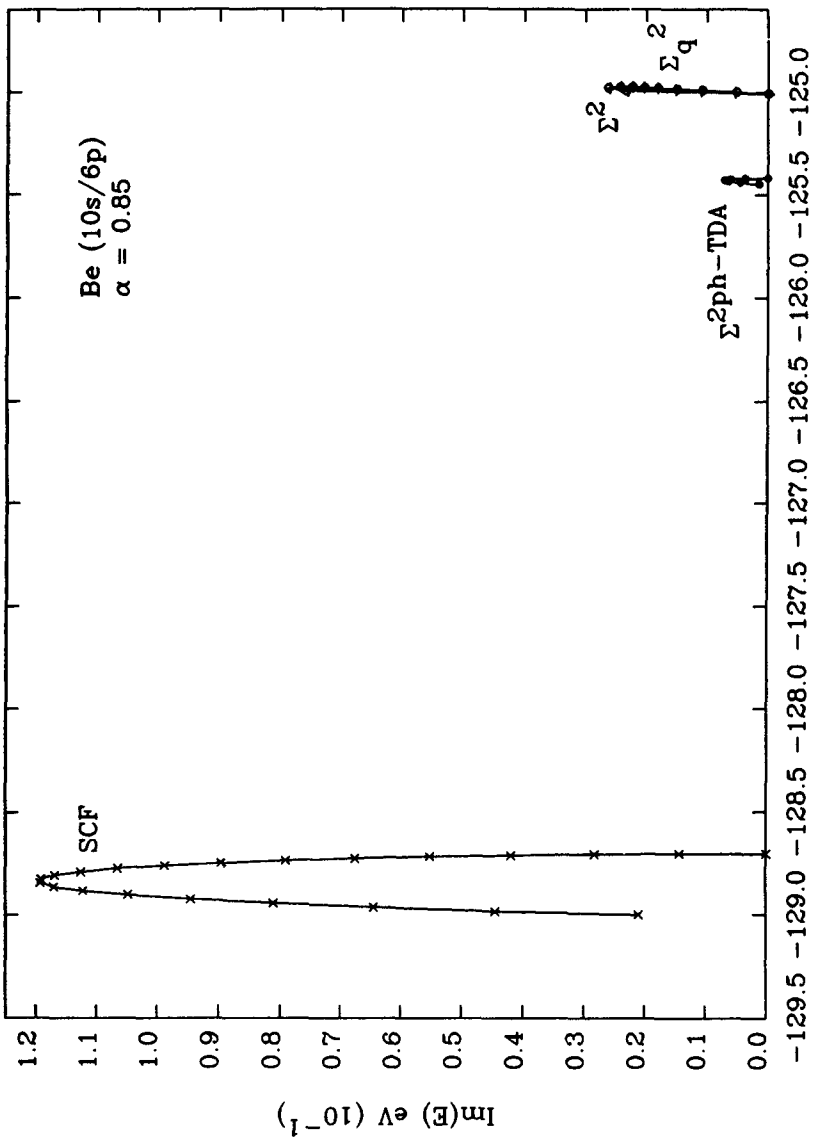

Figure 1. Theta trajectories for the $Be^+(1s^{-1})$ Auger pole from the zeroth (bi-variational SCF), second order (Σ^2), quasiparticle second order (Σ^2_q), diagonal 2ph-TDA ($\Sigma^{2ph-TDA}$) and quasiparticle diagonal 2ph-TDA ($\Sigma^{2ph-TDA}_q$) decouplings of the dilated electron propagator. The disparity between the theta trajectories for the SCF and propagator poles makes apparent the magnitude of correlation and relaxation effects attending the Auger resonance formation.

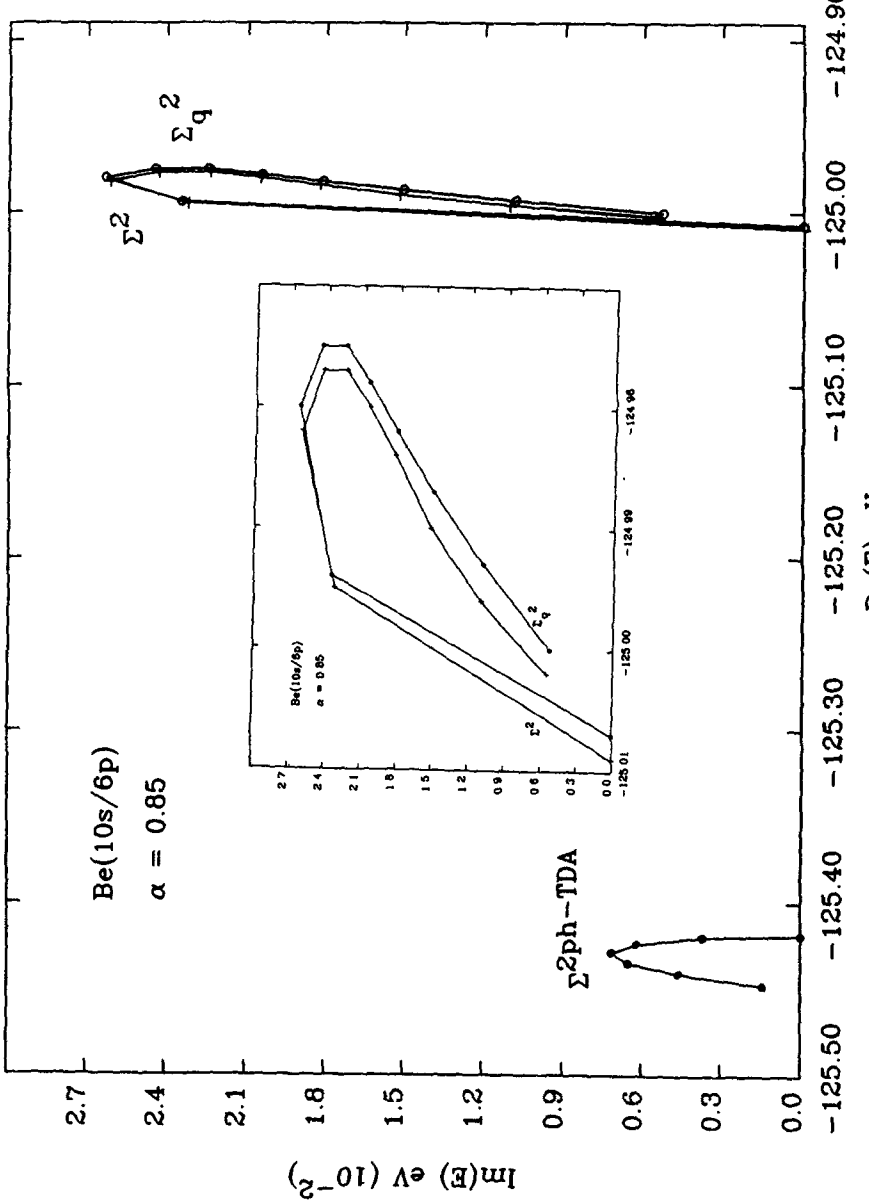

Figure 2. Same as figure 1 but without the zeroth order decoupling. The diagonal 2ph-TDA results predict higher energy and smaller width for the Auger resonance. A magnified version of the second-order (Σ^2), and the quasiparticle second-order (Σ^2_q) trajectories is displayed in the inset.

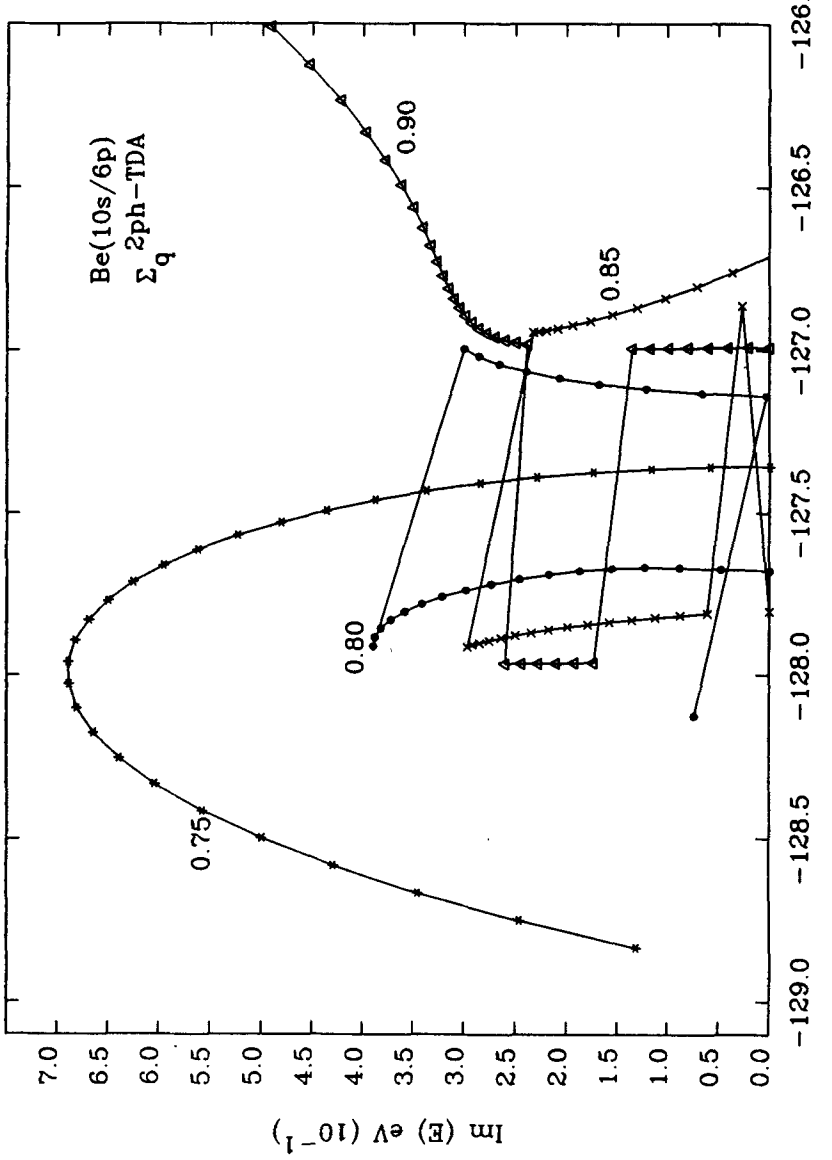

Figure 3. θ trajectories for different values of α for the quasiparticle diagonal 2ph-TDA ($\Sigma_q^{2ph-TDA}$) decoupling. Because of multiple points of quasi-stability for many trajectories, the quasi-stable value of the resonant pole is elicited from the corresponding α trajectory in figure 4.

Table 1. Energy and width of the $Be^+(1s^{-1})^2S$ Auger resonance.

Method reference	Energy (eV)	Width (eV)
Many-body perturbation theory (Kelly 1974)	...	0·09
Electron propagator with Siegert boundary condition (Palmquist *et al* 1981)	125·47	0·02
Experiment (Bisgard *et al* 1978; Rodbro *et al* 1979)	123·63	...
Second-order dilated electron propagator (Mishra *et al* 1983)	124·98	0·05
Quasiparticle second-order dilated electron propagator (this work)	124·98	0·05
Diagonal 2ph-TDA dilated electron propagator (this work)	125·43	0·02
Quasiparticle diagonal 2ph-TDA dilated electron propagator (this work)	127·90	0·54
Zeroth-order dilated electron propagator (this work)	128·80	0·24

The diagonal 2ph-TDA is an apppealing approximation for reasons mentioned earlier and discussed in much greater detail elsewhere (Öhrn and Born 1981; von Niessen *et al* 1984, and references therein). However, it is also known that though it is consistent upto second order, it is incomplete in third and higher orders. This has led to a somewhat mixed result where the diagonal 2ph-TDA does not always offer an improvement over second-order results. The imbalance is compounded by the use of an uncorrelated reference state since many important third- and higher-order diagrams which should have been non-zero become zero in such calculations (Cederbaum and Domcke 1977). This imbalance has been noted by von Niessen *et al* (1984) and Öhrn and Born (1981) have reviewed this with many numerical examples. It is in this context that we call attention to a similar imbalance in the diagonal 2ph-TDA approximation even in the case of dilated electron propagator calculations and that care must be exercised in its use.

As seen from the results discussed earlier, the imbalance in the diagonal 2ph-TDA approximation seems to be aggravated in the present investigation by the quasiparticle approximation to this decoupling. The problem with quasiparticle diagonal 2ph-TDA could be again due to the inconsistent way in which non-diagonal diagrams which contribute to both the initial (2p-h term) and final (2h-p term) state correlations are excluded. This seems to lead, in this case, to a requirement of large rotation pushing the resonant pole higher into the complex energy plane thereby increasing its width in this approximation. The ADC (3) type consistent extended 2ph-TDA decouplings offer obvious advantages but are beyond our computational capability at this time.

A comparison of (4) and (7) makes obvious the somewhat more complicated and expensive nature of the diagonal 2ph-TDA implementation, since the calculation of the denominator shift in (7) necessitates extra calls for recovery of the transformed two electron integrals needed to compute Δ. On the other hand, as evidenced in both figures 1 and 2, as also in table 1, the diagonal quasiparticle approximation which obviates the need for construction of the full non-diagonal self energy matrix (and thereby repeated diagonalizations as well) offers results for the second-order decoupling which is more or less indistinguishable from its much more expensive full non-diagonal counterpart.

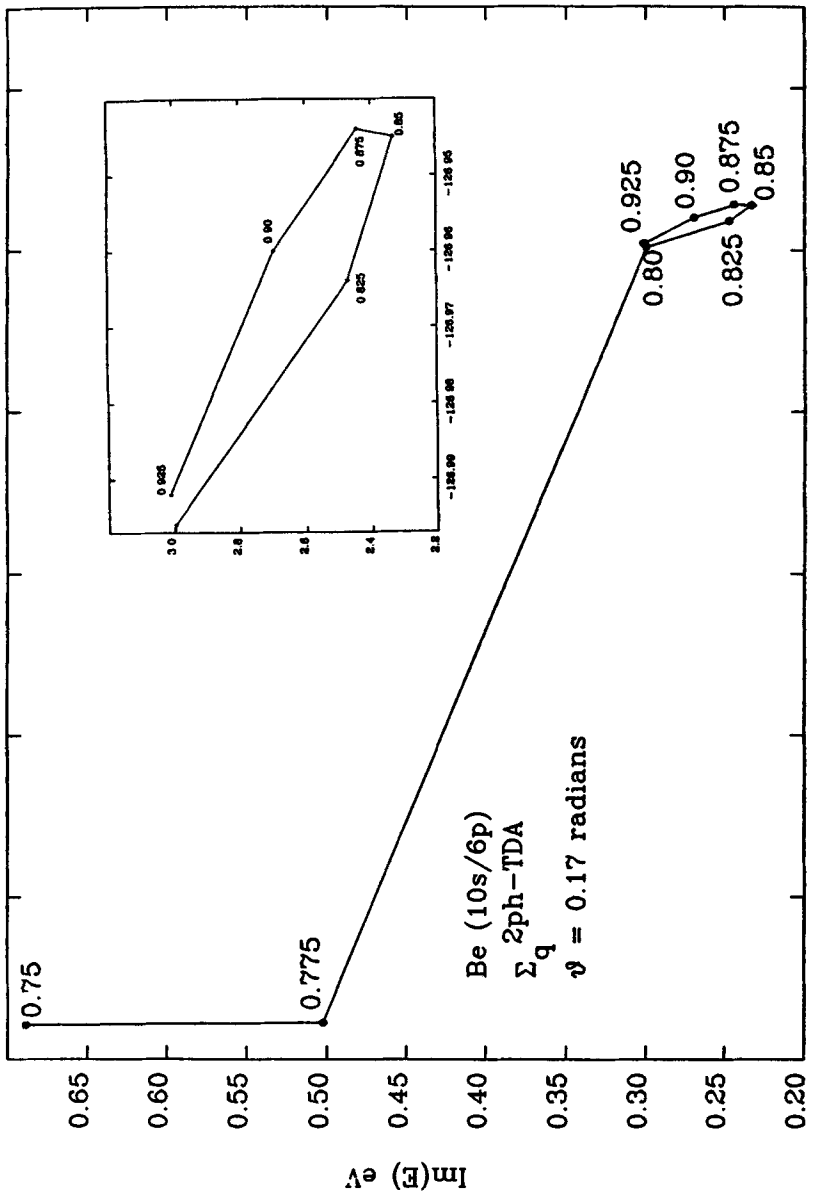

Figure 4. α trajectory for $\theta = 0{\cdot}17$ radians for the quasiparticle diagonal 2ph-TDA ($\Sigma_q^{2ph-TDA}$) decoupling. The distances narrow as $\alpha = 0{\cdot}85$ is approached and then increase again. The quasi-stable value of the pole at this alpha value is therefore taken to be the best estimate of the energy and width of the Auger resonance from this decoupling.

Our results therefore seem to indicate that the extra effort in implementing the diagonal 2ph-TDA approximation for the dilated electron propagator calculations is unwarranted at least from the experience gained in this and some other investigations (Medikeri *et al* 1993, 1994). We should however mention that results presented here are not sufficient by themselves to draw definitive conclusions regarding the techniques used and based on earlier experience (Cederbaum *et al* 1978, 1980) the dilated diagonal 2ph-TDA could be quite effective in the treatment of Auger satellites. These Auger satellites however cannot be investigated using the pole search procedures currently employed for the dilated electron propagator calculations (Donnelly and Simons 1980; Donnelly 1982a; Mishra *et al* 1983a). Iterative diagonalization of the $\mathbf{L}(E)$ matrix where E^{n+1} is selected as the ε_n nearest to E^n automatically locks on to the principal poles and does not permit the treatment of inner valence Auger satellites. The poles may also be searched as complex E values for which

$$\det|\mathbf{G}^{-1}(E)| = \det|E_1 - \mathbf{L}(E)| = 0,$$

but effective algorithms to find zeros of a complex function of complex argument are known to be demanding. The promise of extending the domain of applications of the dilated electron propagator to the treatment of Auger satellites, however, merits serious consideration and an effort along these lines is underway in our group.

Finally, our investigations do seem to indicate that the dilated electron propagator technique may be profitably employed in the investigation of Auger resonances. There is a need for employing consistent 2ph-TDA approximations like the ADC(3) decouplings and while the simplicity of the diagonal 2ph-TDA/diagonal quasiparticle 2ph-TDA decouplings retain the same appeal as in the case of real electron propagator, our results in this case seem to imply that these approximations should be employed with due care. The effectiveness of the quasiparticle second-order approximation even for a core Auger hole calculation, however, is a pleasant surprise and we conclude by recommending this welcome economy in all dilated electron propagator calculations but with an additional caveat that such approximations are known to break down for systems with low symmetry and large number of electrons (von Niessen *et al* 1984) and there is a need to exercise due caution in their use. It is also useful to recall that all quantum chemical calculations are only as good as the quality of the primitive basis set employed. The coordinate space span of the primitive basic set is critical to the description of resonances (Medikeri *et al* 1994). The present basis set was chosen since it has been used in a similar context in a large number of earlier applications (Mishra *et al* 1983a, b; Medikeri *et al* 1993, 1994; Medikeri and Mishra 1993). An exhaustive study of the basis set effects in the characterization of Auger resonances is another obvious extension which is being investigated in our group.

Acknowledgement

This investigation has been sponsored by the Department of Science and Technology through their grant no. SP/S1/F60/88 to MKM. Their support is gratefully acknowledged.

References

Bisgard P, Bruch R, Dahl P, Fatrup B and Rodbro M 1978 *Phys. Scr.* **17** 49

Cederbaum L S 1990 *Int. J. Quantum Chem.* **S24** 393, and references therein

Cederbaum L S and Domcke W 1977 *Adv. Chem. Phys.* **36** 205

Cederbaum L S, Domcke W, Schirmer J and von Niessen W 1980 *Physica Scripta* **21** 481

Cederbaum L S, Domcke W, Schirmer J, von Niessen W, Diercksen G H F and Kraemer W P 1978 *J. Chem. Phys.* **69** 1591

Das A and Melissinos A C 1986 *Quantum mechanics* (New York: Gordon and Breach) p. 534

Donnelly R A 1982a *J. Chem. Phys.* **76** 5414

Donnelly R A 1982b *Int. J. Quantum Chem.* **S16** 653

Donnelly R A 1985 *Int. J. Quantum Chem.* **S19** 337

Donnelly R A 1986 *J. Chem. Phys.* **84** 6200

Donnelly R A and Simons J 1980 *J. Chem. Phys.* **73** 2858

Froelich P and Löwdin P O 1983 *J. Math. Phys.* **24** 89

Herman M F, Freed K F and Yeager D L 1981 *Adv. Chem. Phys.* **48** 1

Holneicher G, Ecker F and Cederbaum L S 1972 In *Electron spectroscopy* (ed.) D A Shirley (Amsterdam: North-Holland)

Ho Y K 1983 *Phys. Rep.* **99** 2

Jörgensen P and Simons J 1981 In *Second quantization based methods in quantum chemistry* (New York: Academic Press)

Junker B R 1982 *Adv. At. Mol. Phys.* **18** 207

Kelly H P 1974 *Phys. Rev.* **A9** 1582

Kurtz H A and Öhrn Y 1978 *J. Chem. Phys.* **69** 1162

Linderberg J and Öhrn Y 1973 In *Propagators in quantum chemistry* (New York: Academic Press)

Löwdin P O, Froelich P and Mishra M 1989a *Int. J. Quantum Chem.* **2** 867

Löwdin P O, Froelich P and Mishra M 1989b *Adv. Quantum Chem.* **20** 185

Medikeri M N and Mishra M K 1993a *Chem. Phys. Lett.* **211** 607

Medikeri M N, Nair J and Mishra M K 1993 *J. Chem. Phys.* **99** 1869

Medikeri M N, Nair J and Mishra M K 1994 *J. Chem. Phys.* **100** 2044

Meyer H D 1989 *Phys. Rev.* **A40** 5605

Meyer H D, Pal S and Riss U V 1992 *Phys. Rev.* **A46** 186

Mishra M 1989 In *Lecture notes in chemistry* (ed.) D Mukherjee (Berlin: Springer-Verlag) vol. 50, p. 223, and references therein

Mishra M 1994 (to be published)

Mishra M, Froelich P and Öhrn Y 1981a *Chem. Phys. Lett.* **81** 339

Mishra M, Goscinski O and Öhrn Y 1983b *J. Chem. Phys.* **79** 5494

Mishra M, Goscinski O and Öhrn Y 1983c *J. Chem. Phys.* **79** 5505

Mishra M, Öhrn Y and Froelich P 1981b *Phys. Lett.* **A81** 4

Mishra M, Kurtz H A, Goscinski O and Öhrn Y 1983a *J. Chem. Phys.* **79** 1896

Öhrn Y and Born G 1981 *Adv. Quantum Chem.* **13** 1

Ortiz J V 1990 *Int. J. Quantum Chem.: Quantum Chem. Symp.* **S24** 585

Ortiz J V 1992 *Chem. Phys. Lett.* **199** 530, and references therein

Ortiz J V and Öhrn Y 1980 *J. Chem. Phys.* **72** 5744

Palmquist M, Altick P L, Richter J, Winkler P and Yaris R 1981 *Phys. Rev.* **A23** 1795

Reinhardt W P 1982 *Annu. Rev. Phys. Chem.* **33** 223

Rodbro M, Bruch R and Bisgard P 1979 *J. Phys.* **B12** 2413

Simons J 1977 *Annu. Rev. Phys. Chem.* **28** 15

Simons J 1978 In *Theoretical chemistry: Advances and perspectives* (ed.) H Eyring (New York: Academic Press) vol. 3

von Niessen W, Schirmer J and Cederbaum L S 1984 *Comput. Phys. Rep.* **1** 57

Winkler P 1979 *Z. Phys.* **A291** 199

Winkler P, Yaris R and Lovett R 1981 *Phys. Rev.* **A23** 1787