

CONTINUUM VERSUS DISCRETIZED WAVEFUNCTIONS. THE IMPORTANCE OF BEING WELL NORMALIZED

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We illustrate, for some resonance widths of helium-like systems, and a Fano-type expression recently proposed, the importance of discretized continuum wavefunctions being well re-normalized. Our conclusions bear on the use of L^2 techniques to evaluate matrix elements such as autoionization and predissociation lifetimes, photoionization probabilities, and unimolecular and bimolecular reaction probabilities.

1. Introduction

A recurrent theme in the literature is the representation of continuum wavefunctions by discretized, L^2 -integrable approximations. Such procedures are widely used in the evaluation of probabilities of predissociation, ionization, unimolecular and bimolecular reactions. They entail no essential difficulty when summation over all continuum states is effected [1], since they are then equivalent to a quadrature of the corresponding integral. However, when specific matrix elements are required, one can obtain non-sensical results if the discretized wavefunctions are not properly re-normalized. Since this does not appear to be widely recognized in the literature, we shall take up a specific example to show the importance of the problem.

A simple solution to this problem of re-normalization of discretized continuum wavefunctions has been proposed by us in a recent publication [2], which complements previous work [3–19] on powerful, but computationally involved, Stieltjes imaging techniques. Since our re-normalization method has been thoroughly tested to be very accurate [20–25], we shall employ it in order to show the importance of correctly normalizing the wavefunctions resulting from a variational treatment, in the context of the Fano-type expression recently used by Komiha et al. [26] to calculate auto-ionization widths.

Atomic units are used throughout, except for resonance widths, which are given in eV.

2. Theory

We have not been able to trace in the literature the Fano-type expression given by Komiha et al. [26], and we shall briefly sketch our proof. In it, we employ a generalization of Fano's [27] pioneer treatment of a discrete atomic state interacting with an adjacent continuum above a single threshold E^* . We shall work in the framework of the well-known Feshbach [28] partitioning of closed- (Q) and open-channel (P) components of an autoionizing wavefunction.

This wavefunction satisfies the Schrödinger equation

$$H\psi = \epsilon\psi \quad (1)$$

and the standard treatment [28] yields (to first order in QHP) the resonance position as the eigenvalue of the projected equation:

$$QHQ\phi_i^d = E_i^d\phi_i^d. \quad (2)$$

The resonance width is given by a golden rule expression:

$$\Gamma = 2\pi |\langle \phi_n^d | QHP | \chi_E \rangle|^2, \quad (3)$$

where the continuum wavefunction χ_E can be con-

structed (to first order in QHP) as the eigensolution of

$$PHP\chi_E = E\chi_E, \quad (4)$$

which has a continuum spectrum for $E > E^*$ and a discrete one (for neutral and positively ionized species) for $E < E^*$.

Let us now suppose that we employ a discretization procedure to calculate χ_E – that is, that we solve eq. (4) within the manifold spanned by a set of L^2 -integrable functions. The resonance condition ($E_i^d = \tilde{E}_n$) can be straightforwardly fulfilled, e.g., by inverse interpolation with respect to a suitable parameter in the basis [20]. It is known [29,30] that discretization provides an approximation $\tilde{\chi}_n$, up to a normalization factor, to the exact P wavefunction χ_E of same energy \tilde{E}_n , in the neighbourhood of the atomic nucleus.

The need for re-normalization of the discretized wavefunctions arises from the fact that they fulfill

$$\langle \tilde{\chi}_n | \tilde{\chi}_m \rangle = \delta_{nm} \quad (5)$$

instead of

$$\langle \chi_E | \chi_{E'} \rangle = \delta(E - E') \quad (6)$$

with $E = \tilde{E}_n$, $E' = \tilde{E}_m$, as is assumed in the deduction of eq. (3). By explicit comparison of the exact and discretized wavefunctions, we proved in ref. [2] that, provided that the basis set is chosen in an appropriate way (e.g. constructed from a set of even-tempered orbitals), the normalization factor is given, to good accuracy, by

$$\chi_E \approx \rho_n^{1/2} \tilde{\chi}_n \approx \left(\frac{2}{\tilde{E}_{n+1} - \tilde{E}_{n-1}} \right)^{1/2} \tilde{\chi}_n. \quad (7)$$

Our method to calculate autoionization widths [20–24] was based on the use of eqs. (3) and (7).

An alternative L^2 procedure to calculate Γ , recently proposed [26], is to perform a discretization of the continuum spectrum of H , yielding an L^2 -integrable approximation $\tilde{\psi}_\alpha$, with energy $\tilde{\epsilon}_\alpha$, to the resonance wavefunction ψ of eq. (1). The particular resonant eigensolution can be picked up from the secular equation eigenvectors and eigenvalues, by using a stabilization technique [29]. Hence, in this approach one solves eq. (2) and a discretized, stabilized version of eq. (1). However, to be able to ap-

ply the golden rule expression (3) for the width, the theory must be further developed. For this, one can use closure of the $P+Q$ states and write

$$\tilde{\psi}_\alpha = \sum_j \langle \phi_j^d | \tilde{\psi}_\alpha \rangle \phi_j^d + \sum_m \langle \tilde{\chi}_m | \tilde{\psi}_\alpha \rangle \tilde{\chi}_m, \quad (8)$$

which holds, to arbitrary accuracy, provided the basis set is large enough (and complete in the limit). Application of the bras $\langle \phi_i^d | H$ and $\langle \tilde{\chi}_n | H$ yields

$$\begin{aligned} \langle \phi_i^d | H | \tilde{\psi}_\alpha \rangle &= \langle \phi_i^d | \tilde{\psi}_\alpha \rangle E_i^d + \langle \tilde{\chi}_n | \tilde{\psi}_\alpha \rangle \langle \phi_i^d | H | \tilde{\chi}_n \rangle \\ &+ \sum_{m \neq n} \langle \tilde{\chi}_m | \tilde{\psi}_\alpha \rangle \langle \phi_i^d | H | \tilde{\chi}_m \rangle, \\ \langle \tilde{\chi}_n | H | \tilde{\psi}_\alpha \rangle &= \langle \phi_i^d | \tilde{\psi}_\alpha \rangle \langle \tilde{\chi}_n | H | \phi_i^d \rangle + \tilde{E}_n \langle \tilde{\chi}_n | \tilde{\psi}_\alpha \rangle \\ &+ \sum_{j \neq i} \langle \phi_j^d | \tilde{\psi}_\alpha \rangle \langle \tilde{\chi}_n | H | \phi_j^d \rangle, \end{aligned} \quad (9)$$

wherefrom, by straightforward algebra, and eliminating terms quadratic in QHP , we obtain

$$(\tilde{\epsilon}_\alpha - E_i^d) \langle \phi_i^d | \tilde{\psi}_\alpha \rangle = \langle \tilde{\chi}_n | \tilde{\psi}_\alpha \rangle \langle \phi_i^d | H | \tilde{\chi}_n \rangle. \quad (10)$$

Squaring both members of this equation and summing over the discretized “continuum” spectrum of H :

$$\begin{aligned} \sum_{\alpha} (\tilde{\epsilon}_\alpha - E_i^d)^2 \langle \phi_i^d | \tilde{\psi}_\alpha \rangle^2 \\ (\tilde{\epsilon}_\alpha > E^*) \\ = \langle \phi_i^d | H | \tilde{\chi}_n \rangle^2 \sum_{\alpha} \langle \tilde{\chi}_n | \tilde{\psi}_\alpha \rangle \langle \tilde{\psi}_\alpha | \tilde{\chi}_n \rangle \\ (\tilde{\epsilon}_\alpha > E^*) \end{aligned} \quad (11)$$

with $\tilde{\epsilon}_\alpha > E^*$. Now, since the entire spectrum of H contains a Rydberg part,

$$\begin{aligned} \sum_{\alpha} |\tilde{\psi}_\alpha \rangle \langle \tilde{\psi}_\alpha| &= 1 - \sum_{\alpha} |\tilde{\psi}_\alpha \rangle \langle \tilde{\psi}_\alpha| \\ (\tilde{\epsilon}_\alpha > E^*) &(\tilde{\epsilon}_\alpha < E^*) \\ \approx 1 - \sum_m |\tilde{\chi}_m \rangle \langle \tilde{\chi}_m|. \end{aligned} \quad (12)$$

Substitution in eq. (11) yields

$$\langle \phi_i^d | H | \tilde{\chi}_n \rangle^2 = \sum_{\alpha} (\tilde{\epsilon}_\alpha - E_i^d)^2 \langle \phi_i^d | \tilde{\psi}_\alpha \rangle^2 \quad (\tilde{\epsilon}_\alpha > E^*) \quad (13)$$

and from (3), (6), (7) we obtain the sought-for alternative expression [26] for Γ :

$$\Gamma = 2\pi\rho_n \sum_{\alpha} (\tilde{\epsilon}_\alpha - E_i^d)^2 \langle \phi_i^d | \tilde{\psi}_\alpha \rangle^2, \quad (\tilde{\epsilon}_\alpha > E^*) \quad (14)$$

which involves the variance, with respect to ϕ_i^d , of H . This expression differs from that of Komiha et al. [26] in the appearance of a re-normalization factor ρ_n . We see no way to calculate it without solving eq. (4). Hence, and contrary to what is indicated by those authors, there seems no alternative, in the golden rule approach, to solving the open-channel equation, whether it be in a numerical or discretized version. We illustrate in section 3 the consequences of neglecting the ρ_n factor in eq. (14).

3. Illustration of the importance of being well normalized

Since our tests [20–24] on the accuracy of eq. (7) have been mainly performed for atomic systems, we have applied our treatment to the lowest two ¹S resonances of the He atom and the helium-like ions B³⁺ and Ne⁸⁺. The basis sets employed are the same as in ref. [23]. For the stabilization treatment of eq. (1), we have just added to the closed-channel basis set the hydrogen-like orbital corresponding to the pertinent ionized system (He⁺(1s), B⁴⁺(1s), Ne⁹⁺(1s)). We have found expression (14) to be numerically unstable for the largest eigenvalues $\tilde{\epsilon}_\alpha$, since the corresponding terms are products of very small overlaps times very large energy differences, so that some care must be exercised in its evaluation.

The results of employing our discretization method, and those of using eq. (14) with ρ_n set equal to one, are compared in table 1, together with the accurate values reported for He in complex rotation

[31] and close coupling [32] calculations.

From table 1, we see that for He, eq. (14) with $\rho_n=1$ gives resonance widths of the right order of magnitude. However, this strongly depends on the basis set [2], and there is no reason to expect this coincidence in the general case: comparison for the cases of B³⁺ and Ne⁸⁺ clearly illustrates this point. The Z^2 increase obtained by taking $\rho_n=1$ in eq. (14) is in clear contradiction with the results of accurate calculations, and a Z^{-1} expansion of the resonance widths [24].

It should be emphasized that neglect of the corresponding ρ_n in eqs. (3) and (7) would lead to similar non-sensical results for B³⁺ and Ne⁸⁺. To bring forth this point more quantitatively, we also include the value of ρ_n from our calculations [23]. The main problem with eq. (13) is that there is no way of estimating the re-normalization factor ρ_n from the stabilization data alone. Of course, one can evaluate it if eq. (4) is also solved; in earlier work [33] a constrained-variation approach was proposed, and successfully employed [33,34], to solve eq. (4) after a stabilization determination of the resonance state, and thus obtain ρ_n .

4. Conclusion

In this work we have emphasized the importance that discretized continuum wavefunctions be well re-normalized, for their use in the evaluation of matrix elements such as autoionization lifetimes.

In particular, we have shown how ignorance of the

Table 1

Illustration of the consequence of neglecting the normalization factor ρ_n in eq. (7). E is the position of the two lowest ¹S resonances; (a) the widths obtained in ref. [23] through a discretization of the Feshbach open-channel equation; (b) the results of eq. (14) with $\rho_n=1$; (c) the complex rotation [31] data; (d) the close-coupling [32] data. We also include the value of ρ_n for our Feshbach calculation. It should be noticed that this value of ρ_n is different from that which would apply in the procedure of Komiha et al. [26] and which cannot be obtained from stabilization data alone

	E	ρ_n	a	b	c	d
He	-0.7784	1.21	0.123	0.218	0.123	0.125
	-0.6193	1.08	0.008	0.020	0.006	0.006
B ³⁺	-5.6621	0.19	0.177	1.677		
	-5.1336	0.18	0.010	0.216		
Ne ⁸⁺	-23.798	0.048	0.194	6.74		
	-22.660	0.046	0.011	0.930		

proper normalization factor precludes the use of the Fano-type approach recently proposed by Komiha et al. [26], and which employs a stabilization treatment for the electronic Hamiltonian, together with a solution of the Feshbach closed-channel equation. Comparison with accurate data shows that orders-of-magnitude errors can be obtained unless the normalization factor happens to be close to unity.

In recent work [2,23,24,35] we have analyzed in detail this problem of unknown normalization in discretized wavefunctions, and shown that a simple solution exists (eq. (7)), provided the basis set used to solve the open-channel equation is appropriately chosen. This permits the use of either Feshbach partitioning with discretization of the open-channel spectrum [20–24], or stabilization together with a constrained-variation solution of the open-channel equation [33,34].

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