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A SIMPLE APPROACH TO PREDICTING RESONANCE LEVELS

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We propose a modification of Hazi and Taylor's stabilization method for calculating resonance energies by adding a positive definite operator to the hamiltonian. The purpose of this operator is to raise the energies of scattering states while not significantly affecting the bound or resonance states. The method has advantages over the ordinary stabilization techniques. We treat two model problems and discuss possible applications to atomic and molecular systems.

1. Introduction

In principle, the Schrödinger equation, $H\psi = (\hat{T} + \hat{V})\psi = E\psi$, and its accompanying eigenfunctions and eigenvalues are uniquely described by the potential energy, V [1]. For any V, we may define three different types of eigenfunctions and eigenvalues [2]. The first type are bound state solutions having energy below that of the component species separated to infinity. For example, the 1s, 2s, 2p, 3s, 3p, ... energy levels for the hydrogen atom ($V = -e^2/r$) problem. All of the other states have positive energy and are referred to as continuum states. For many problems we find a further taxonomic division is useful. There may be solutions with energy above the separated particle energy, but still lower than a potential energy maximum. (These states are nonetheless not square integrable.) The corresponding eigenfunctions may be nearly bound and quite localized in the potential well. These states are called resonance states, while the more delocalized states with arbitrary positive energy are called scattering states. For example, the "semi-empirical" [3] potential

$$V(r) = -\alpha/2r^4 + l(l+1)/2r^2 ,$$

where α is the polarizability of the atom and l the angular momentum state of the added electron ($l = 0$, s; $l = 1$, p; etc.) is used to approximate a potential energy "barrier" which can temporarily bind an additional electron.

The physical properties of resonance states are very different from scattering states [3]. For example, they are much longer lived. Accordingly, we are led to the question of deciding if a given calculated continuum state is a resonance or scattering state. A frequently employed approach is Hazi and Taylor's stabilization method [4]. A basis of square integrable functions $\{\psi_k\}$ is chosen and the representation of the hamiltonian, within this basis is diagonalized. A resultant eigenvalue, E_α, and eigenvector C_α are judged to be stabilized if, as the basis is chosen to be more and more complete by expanding the basis set (or systematically varying orbital exponents), the eigenvalue E_α remains essentially unchanged. As Hazi and Taylor have shown, stable roots of the secular equation correspond to bound state or resonance state solutions. Solutions whose roots are not stable correspond to approximations to the scattering eigenfunctions of H.

The truly bound eigenstates of H can be approximated in a straightforward and well-understood manner, the Rayleigh–Ritz variational principle and the accompanying Hylleraas–Undheim theorem [5]. The corresponding calculation of continuum states, both

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resonance and scattering, is complicated by the problem of variational collapse, i.e. below any continuum state there is an infinite number of other states. As such, there is a major difficulty in the stabilization technique: it is necessary to do numerous calculations for any problem of interest. It is well-known that the expense of a calculation increases dramatically with the size of basis set chosen [6]. Accordingly, the necessity of performing calculations with ever larger sets may simply be economically unfeasible for the basis sets of interest. This seems surprising noting the extensive literature involving large configuration interaction (CI) studies [6]. The standard procedures for determining the approximate eigenfunctions and eigenvalues or energy levels of large matrices provide only the first few values [7]. This is sufficient for most systems studied by CI techniques. However, we are not looking for the lowest energy solutions but for those that are stabilized. Accordingly, with the usual stabilization method, we must look at numerous eigenvalues and we must examine how they change with changes in the basis set.

In this paper we wish to present an alternative technique for studying resonance states. Rather than minimizing the expectation value of H, we will instead take the functional derivative of

$$E'[\psi] = \langle\psi|H + \Omega|\psi\rangle/\langle\psi|\psi\rangle , \tag{1}$$

where the positive operator Ω has been chosen so that its expectation values are small for bound and resonance states but large for scattering states. This will allow us to look for just the lower eigenvalues of expression (1), as in the above mentioned CI calculations, because the scattering states will have been removed from the low-energy spectrum. We now discuss possible choices of Ω and examine in more detail how the method is implemented.

2. Implementation of the method

Let us now discuss how to choose Ω and the consequences of minimizing expression (1). We wish to have an added functional $\langle\Omega\rangle$ that is small for the bound or localized resonance states but large for scattering states. This suggests that Ω should be positive definite as to prevent the possibility of an eigenfunction of (1) having an eigenvalue that is lower than a real *bound* state. Localized states may be expected to have small values of $\langle r^s\rangle$ (at least for small square integrable basis sets). This suggests that κr^s with appropriate choices of the (small) scale factor κ and (large) exponent s can be used to accomplish the above distinction between resonance and scattering states.

A more quantitative statement of this philosophy is that the stationary points of the functional

$$E'[\psi] \equiv \langle\psi|-\tfrac{1}{2}\nabla^2 + V(r) + \kappa r^s|\psi\rangle/\langle\psi|\psi\rangle \tag{2}$$

should be nearly equal to the localized stationary points of the functional with $\kappa = 0$. The stationary points of $E'[\psi]$ corresponding to nonlocalized functions should be higher in energy than the corresponding stationary points of $E'[\psi]$ for $\kappa = 0$. Indeed, the resultant separation of localized (low-eigenvalue) and non-localized (high-eigenvalue) states is the most important aspect of the approach described here.

If the trial function ψ is approximated as a linear combination of square integrable basis functions ϕ_k $(k = 1, 2, \ldots m)$

$$\psi = \sum_k c'_k \phi_k , \tag{3}$$

the condition that $E'[\psi]$ reach an extremum can be expressed as follows

$$\sum_{l=1}^{m} [\langle\phi_k|-\tfrac{1}{2}\nabla^2 + V(r)|\phi_l\rangle + \kappa\langle\phi_k|r^s|\phi_l\rangle]\, c'_{l,\alpha} = \sum_l \langle\phi_k|\phi_l\rangle c'_{l,\alpha} E'_\alpha . \tag{4}$$

Once the eigenvalues and eigenvectors of eq. (4) belonging to localized (bound or resonance) states are obtained (these are presumably the lowest lying energy states and relatively few in number), we can use a perturbation theory [2] approach to remove from the eigenvalue E'_α the effects of the artificial "external potential" κr^s. First order Rayleigh–Schrödinger perturbation theory approximates the desired (localized) eigenvalue (E_α) of H as

$$E_\alpha \equiv E'_\alpha - \sum_{i,j=1}^{m} c'_{i\alpha} c'_{j\alpha} \langle\phi_i|r^s|\phi_j\rangle\kappa . \tag{5}$$

Although we may be able to go to higher orders in perturbation theory we feel that for the localized states of H' it is adequate to stop at this first-order expression because of the small effect of κr^s on such states. Of course, eq. (5) is not used to generate corrections to the scattering states of H' because we are not interested in these states.

3. Solutions of the model problem

We return to Hazi and Taylor's paper [4] and note their one-dimensional model problem useful for simulating atomic shape resonance potentials. These authors solved for eigenstates of the model potential

$$\begin{aligned} V(x) &= \tfrac{1}{2}x^2\,, & x \leqslant 0; \\ &= \tfrac{1}{2}x^2 \exp(-\lambda x^2)\,, & x \geqslant 0\,, \end{aligned} \qquad (6)$$

with $\lambda > 0$, both by numerical integration of the Schrödinger equation and by making a finite basis set expansion of the wavefunction $\psi(x)$. Noting the similarity of the potential with that of the harmonic oscillator [2], these authors used the eigenfunctions of the latter problem as the basis set for the former.

We solved for the eigenstates of a related potential

$$\begin{aligned} V(x) &= \tfrac{1}{2}x^2\,\theta(-x) \\ &\quad + [\tfrac{1}{2}x^2 \exp(-\lambda x^2) - J\exp(-\lambda x^2) + J]\,\theta(x)\,, \end{aligned} \qquad (7)$$

where λ and J are constants and $\theta(x)$ is the Heaviside step function $[\theta(x) = 1, x > 0; \theta(x) = 0, x < 0]$. For $J = 0$, we recover the Hazi–Taylor potential. For $J > 0$, the Hazi–Taylor potential is modified so that the potential energy approaches J as $x \to \infty$. Accordingly, there is now the possibility of having bound states in addition to resonance and scattering continuum states. A nonzero "external potential" κx^s is then added to $V(x)$ to "decide" between the resonance and scattering states. The obvious problem is how to choose κ and s. If κ is too small for a certain s, then the effect on the non-resonant continuum states will not be very large. In such cases several true continuum states may lie below the resonance state(s) and little would be gained by so modifying the potential. Contrariwise, if κ is too large then both the bound and resonance energies will also be changed significantly from their respective values when the "external potential" κx^s is turned off. First-order perturbation theory may then not be sufficient to correct the energies.

We have found the following procedure to be useful in choosing these important parameters. Optimal values of κ are determined from the position of the maximum value of V for positive x [the right-hand hill height of $V(x)$], $x_{\max} = (2J + 1/\lambda)^{1/2}$ as follows:

$$\kappa = [c^{s/2}\,(2J + 1/\lambda)^{s/2}]^{-1}\,, \quad c \geqslant 1\,.$$

States which, for $\kappa = 0$ had large amplitudes outside of the potential maximum, $x_{\max}$, will have significantly larger energies when $\kappa \neq 0$. States which had large amplitudes inside the potential should be much less affected.

In fig. 1 we show the Hazi–Taylor ($J = 0, \lambda = 0.19$) potential for the cases ($\kappa = 0$) and ($s = 8, \kappa = 8.1 \times 10^{-5}$). The eigenvalues of both potentials shown by horizonal lines are the lowest four eigenvalues for the secular matrix derived from a basis consisting of the lowest forty Hermite polynomials. The eigenvalues, expectation values of x^2, and first-order corrected eigenvalues of eq. (5) are given in table 1.

The "stabilized" resonance root has an energy of approximately 0.45. It is the second lowest root of the unmodified 40 × 40 case. However, by evaluating the expectation value of x^2 for the two lowest roots (the scattering state and the desired resonance state) we find the following useful fact: the state at $E = 0.1797$ is very diffuse having $\langle x^2 \rangle = 40.2428$ while the higher-lying state with $E = 0.45$ has $\langle x^2 \rangle$ of the low-lying eigenstates of H, we can determine that the state of 0.1797 is not a resonance state.

Modifying the Hazi–Taylor potential by adding an

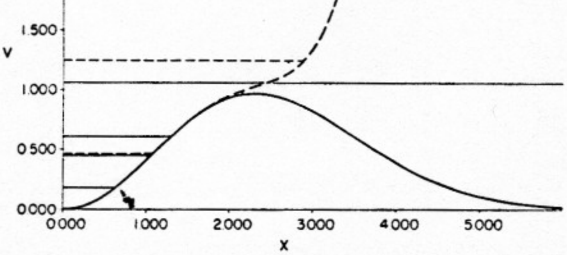

Fig. 1. The Hazi–Taylor potential and associated eigenvalues (solid lines) plus the ($s = 8$, $\kappa = 8.1 \times 10^{-5}$) modified Hazi–Taylor potential and associated eigenvalues (dashed lines) for the 40 × 40 case.

Table 1
Roots of the 40 × 40 secular equation. Columns 2 and 3 refer to the ordinary Hazi–Taylor model potential ($J = 0$, $\kappa = 0$, $\lambda = 0.19$) while the potential of columns 4, 5, and 6 are modified with $\kappa = 0.000081$ and $s = 8$

	E a)	$\langle x^2 \rangle$	E'	E b)	$\langle x^2 \rangle$
root 1	0.1797	40.2428	0.4582	0.4558	0.6403
root 2	0.4526	1.2282	1.2434	1.1928	2.6124
root 3	0.6052	33.9139	1.9132	1.7401	3.9961
root 4	1.0578	20.1351	2.7252	2.4570	4.2974

a) For the $\kappa = 0$ case.
b) From eq. (5).

Table 2
Roots of the 40 × 40 secular equation. Columns 2 and 3 refer to a potential with $J = 0.8$, $\lambda = 0.19$, and $\kappa = 0$ while the potential of columns 4, 5, and 6 are modified with $\kappa = 0.000028$ and $s = 8$

	E a)	$\langle x^2 \rangle$	E'	E b)	$\langle x^2 \rangle$
root 1	0.5016	0.4874	0.5019	0.5016	0.4846
root 2	1.3711	38.5831	1.5205	1.5128	1.8722
root 3	1.5076	3.8845	2.2584	2.1767	0.4377
root 4	1.7753	31.4735	2.9366	2.7292	5.5658

a) For the $\kappa = 0$ case.
b) From eq. (5).

"external potential" of $0.000081\, x^8$ causes significant changes in the energy spectrum. For the 40 × 40 case, the lowest root of H' is the stable resonance state at 0.45. The more diffuse states lie at considerably higher energies. For example, the next lowest state is at an energy of 1.19. For this simple model potential the problem of contamination of the low-lying roots by continuum states described within a discrete square-integrable basis causes no serious difficulties. The technique of adding κx^s shifted the unwanted scattering states to higher energies.

The results of a second example are shown in fig. 2 and table 2. In this case the state at 0.50 au is a bound state and the state at 1.5 is a very broad resonance. (This state is broad because it lies close to the top of the potential $V(x)$.) For the 40 × 40 diagonalization with $\kappa = 0$, a continuum state is the second lowest root. With $\kappa = 2.8 \times 10^{-5}$ and $s = 8$, the second lowest state corresponds to the resonance state. More diffuse states lie at much higher energies; again the method has been successful.

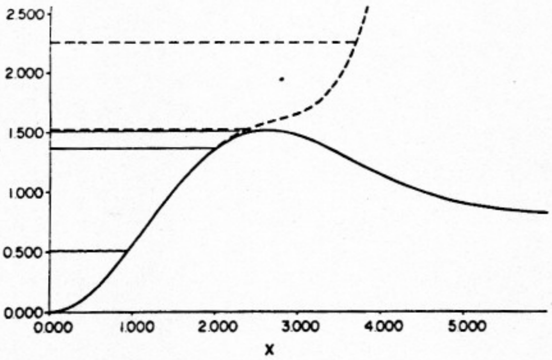

Fig. 2. The potential given in eq. (7) ($J = 0.8$, $\lambda = 0.19$) and the associated eigenvalues (solid lines), plus the modified ($s = 8$, $\kappa = 2.8 \times 10^{-5}$) potential and its associated eigenvalues (dashed lines) for the 40 × 40 case.

In table 3 we show results for this same potential with $J = 0.8$, $\lambda = 0.19$ for various values of κ, s being chosen again as 8. The $\mathbf{H}'$ matrix is formed using the lowest fifteen Hermite polynomials as basis functions. As κ is changed from 10^{-1} to 10^{-6}, the energies of the bound and resonance states do not change much nor do their values of $\langle x^2 \rangle$. However, both the energies and $\langle x^2 \rangle$ change drastically for the non-resonance continuum states. These observations suggest the following modification of the usual stabilization techniques.

For a fixed basis set size, a few calculations are done for which κ ranges from large to small values. In these calculations it is important that the basis set include sufficient diffuse functions to permit an adequate description of continuum states. The eigenvalues and $\langle x^2 \rangle$ for bound and resonance states will not change significantly as κ changes, in contrast to scattering states.

For small κ there may be continuum states having large $\langle x^2 \rangle$ which lie below or among the resonance states. However as κ attains larger values, such continuum states can easily be identified by their large changes in $\langle x^2 \rangle$. This identification of the continuum states is the primary purpose of carrying out a calculation at a relatively large value of κ. The calculation at small κ, for which the perturbation is small, is to be used, together with perturbation theory, to evaluate the energies and $\langle x^2 \rangle$ of bound and resonance states. An advantage of applying this method to atoms and molecules is that, for a given basis set, the integrals

Table 3
Roots of the 15 × 15 secular equation. $J = 0.8$, $\lambda = 0.19$, $s = 8$. κ ranges from 0.1 to 0.000001. These energies include the perturbation correction

	$\kappa = 10^{-1}$	$\kappa = 10^{-2}$	$\kappa = 10^{-3}$	$\kappa = 10^{-4}$	$\kappa = 10^{-5}$	$\kappa = 10^{-6}$
root 1	0.5607	0.5132	0.5031	0.5018	0.5017	0.5017
root 2	1.9317	1.6515	1.5502	1.5197	1.5092	1.5049
root 3	3.6528	2.8325	2.4468	2.2763	2.0776	1.9027
root 4	5.3887	4.2444	3.4658	2.9872	2.5207	2.3810

over SCF orbitals need be computed only once regardless of the range of κ studied. In the conventional stabilization technique the basis size (or nature) must be varied, thereby necessitating repeated integral transformation.

Although the results of our model potential studies are encouraging, things are clearly more complicated for atoms and molecules. The electronic hamiltonian could be modified by addition of a function $\kappa_1 x^{s_1} + \kappa_2 y^{s_2} + \kappa_3 z^{s_3}$ where the exponents are even integers. Clearly for atoms $\kappa = \kappa_1 = \kappa_2 = \kappa_3$, and $s = s_1 = s_2 = s_3$. Optimal values of κ can be chosen in several different ways. The first is to choose κ so that states with $\langle r^2 \rangle$ less than $r_{\max}^2$ where $r_{\max} = [2\alpha/2l(l+1)]^{1/2}$, are not significantly affected by our perturbation while those states with $\langle r^2 \rangle$ greater than $r_{\max}^2$ will be markedly changed. To accommodate the anisotropy of molecules κ_1, κ_2, and κ_3 may be chosen by using the diagonal tensorial components of the polarizability: $\alpha_{xx}, \alpha_{yy}, \alpha_{zz}$. Alternatively, one can use the expectation value of r^2 (or for molecules x^2, y^2, and z^2 which are related to components of the quadrupole moment) for the electronic ground state of the target (which is bound and hence localized) to determine κ (or $\kappa_1, \kappa_2, \kappa_3$) as discussed above.

Once κ is chosen, for our scheme to work, the basis must include functions ϕ_i for which $\kappa\langle\phi_i|r^s|\phi_i\rangle$ is both large and small. This restriction on the basis guarantees that localized functions for which $\kappa\langle r^s\rangle$ is small will be adequately described and that nonlocalized scattering functions for which $\kappa\langle r^s\rangle$ is large will have much larger eigenvalues than for the case with $\kappa = 0$. Thus these scattering states will not be among the lowest few eigenvalues of H'.

4. Conclusion

We have proposed and tested on simple one-dimensional models a method for identifying resonance eigenstates. The method exploits the different spatial characteristics of localized (bound or resonance) states and nonlocalized (scattering) states to remove from the low energy spectrum of the hamiltonian the unwanted scattering states in favor of the desired bound and resonance states. As a result of shifting the scattering states to higher energy, we need only compute the lower eigenvalues of the (modified) hamiltonian matrix to find the resonance states. The proposed method is successfully applied to model problems which simulate the behavior of atomic shape resonances. However, the usefulness of our approach cannot be adequately measured by its success in model situations. We are now in the process of applying our modification of the stabilization technique to investigations of shape resonances in atomic and molecular systems. The outcome of these future studies will allow us to better determine the value of our proposed method.

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