

Optimal Basis Functions for Siegert Resonance State Representation in Al₂ Electronic Predissociation

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ABSTRACT. We compare the relative usefulness of common basis functions and numerical integration methods in representing complex resonance state encountered in the molecular scattering problem of aluminum dimer electronic predissociation. Specifically, the basis set size and computing CPU times are monitored in order to find the minimum requirement for ensuring the modest accuracy of calculated resonance energies (0.1 cm^{-1}) for more than 100 resonance states. The combination of the so-called one-dimensional box eigenfunctions and energy-dependent boundary functions are found to be most efficient if integration is done using the basis set quadrature rules.

Key words: Quantum, Molecular, Scattering

INTRODUCTION

The general factors to consider for quantum calculations include the core memory and the CPU time requirements. It is important to choose proper parameters because if they are too demanding, the calculation may be practically impossible. If using basis representation like ‘Efficient Siegert resonance energy calculation method’ (e.g., see ref. 1), those requirements are directly depending on the basis set size.

The quantum mechanical wavefunctions in the continuum region of energy can be represented by suitable basis functions defined on a finite range of scattering coordinate. In the above approach, the basis functions are composed of two different classes.

Most of the basis functions are the ‘bound-type’ ones commonly used for representing bound states, and the remaining basis functions are the so-called ‘boundary function’ which is essential for continuum calculations.

When the computational resources are unlimited, Lobatto shape functions are used for bound-type part supplemented with scattering-energy-independent linear functions. Because of their dense basis density characteristics near the boundaries, very accurate results can be obtained if fully converged. In the other case where they are limited, one-dimensional box eigenfunctions are used with scattering-energy-dependent free waves giving sufficiently reliable results, if not exact.

The purpose of this work is to clarify the relative usefulness of the above-mentioned various combinations of

calculational parameters regarding the choice of basis functions and, also, the numerical integration methods (used for calculating matrix elements) within an identical framework of quantum scattering problem which is an electronic predissociation in this work.

The fate of the electronically excited diatomic molecule is relevant to some interesting chemical problems like the broadening of spectral lines and the mechanism of exciplex lasers. For aluminum dimer, we reported very accurate resonance energies and lifetimes using formally exact quantum calculation method.¹ The present and the previous works are based on the results of the Yarkony group report. They calculated ab initio potential energy surfaces and nonadiabatic coupling terms for the lower 4 electronic states and used them to calculate radiative and radiationless lifetimes of excited states within the Born-Oppenheimer approximation.² This study of radiationless lifetime constitutes a three-coupled one-dimensional potential energy surface (PES) scattering problem with one open channel, not involving the ground bound PES because of selection rules.

METHODS

For the present problem, the Schrödinger equation modified by the Bloch operator L for a Siegert resonance state (of wavefunction ψ_s , energy E_s , and the corresponding complex wavevector k_s) is given by³

$$(H + L - E_s)\psi_s = 0 \quad (1)$$

where

$$L = |\phi_1\rangle \frac{\hbar^2}{2m} \delta(R-p) \left(\frac{d}{dR} - ik_s \right) \langle \phi_1|,$$

$$E_s = \frac{\hbar^2 k_s^2}{2m} + V_{11}(p), \quad k_s = k_r - ik_i$$

The Hamiltonian for the present three channel problem is given by

$$H = -\frac{\hbar^2}{2m} \frac{d^2}{dR^2} + \sum_{i,j=1,3} |\phi_i\rangle V_{ij} \langle \phi_j|$$

where we use diabatic representation of potential energy surfaces and off-diagonal potential couplings (V_{ij}). The Siegert resonance wavefunction ψ_s is expanded by a *boundary function* v for the open channel ϕ_1 and by the *direct product* basis composed of an *bound-type* basis set $\{u_i; i=1, N\}$ and three diabatic electronic states $\{\phi_i; i=1, 3\}$ as

$$\psi_s = \sum_{i=1, N; j=1, 3} C_{ij} |u_i\rangle |\phi_j\rangle + C_0 |v\rangle |\phi_1\rangle$$

where v increases from zero at the proper inner boundary and reaches one at the outer boundary p while u_i 's vanish at both ends. Therefore, total basis functions are $3N + 1$ with $3N$ bound-type functions and one boundary function. The role of L is to impose ψ_s purely outgoing and asymptotically diverging at and near the basis set outer boundary. The complex energy E_s is related with the real resonance energy E_r and lifetime τ by

$$E_s = E_r - i\frac{\Gamma}{2}, \quad \tau = \frac{\hbar}{\Gamma}$$

and the corresponding complex wavevector k_s is composed of real and imaginary parts, k_r and $-ik_i$ respectively.

The atomic separation is denoted by R and the reduced mass 13.490769 amu is by m . The 112 resonance solutions in the energy range from 23,000 cm⁻¹ to 37,000 cm⁻¹ are calculated one by one using the above-mentioned efficient iterative method starting from the initial guesses given by the eigensolutions of Hamiltonian matrix represented by the subset of the direct product basis excluding $|v\rangle |\phi_1\rangle$. Also we conveniently choose discrete variable representation (DVR) for one-dimensional box eigenfunctions where each basis function appears as an approximate delta function centered at Gaussian quadrature points distributed evenly across the basis range. Lobatto shape functions are also in this convenient form for DVR and used accordingly.⁴ The above eigenvectors of the above subset-Hamiltonian matrix serve as bound-type bases throughout the remaining part of calculations. Therefore, the matrix elements which does not involving the boundary

function were evaluated with basis set quadrature rules, which is the most time-saving. On the other hand, different quadrature rules for integrations are tested to obtain matrix elements involving the boundary function. More details of the calculation method and the system may be found elsewhere.^{1,5}

In this work, we focus on finding a compact calculation scheme *with moderate accuracy* rather than pursuing numerically exact solutions. In particular, we compare the relative performance of the Lobatto shape functions (in short, *LOB* in this work) and one-dimensional box eigenfunctions (in short *SIN* in this work) as *bound-type basis*; linear fixed function ($v=F$) and energy-dependent function of a form $g(R)\exp(ikR)$ ($g(r)$ is a cutoff function behaving like v) as *boundary function*; and, quadrature rules based on basis set (in short, *B* in this work) and Lobatto shape functions (in short, *D* in this work) used for *integration method*, respectively. The wavevector k is either determined from the corresponding real eigenenergy of the above bound-type Hamiltonian matrix (in this case $v=W$) or from the calculated approximate complex resonance energy (in this case, $v=X$). The F requires one-time evaluation of integrals while the W and X requires re-evaluation for each resonance state.

Regarding the quadrature rules, B is the most CPU time saving because the basis functions and the quadrature points are identical the integration reduces to a single-index summation while D requires a triple-index summation running for quadratures, Hamiltonian eigenvectors, and the DVR transformation vectors, respectively, for *SIN* case. This property comes from the delta function character inherent in the DVR basis. Those various choices were used before for calculation of model system (except $v=X$ which is newly tested here), however, it is the first time to be applied for a realistic system.⁵

RESULTS

The basis set range for scattering coordinate is chosen as [3.5 Å, 12.5 Å] which is large enough for sufficiently converged results.¹ To compare the relative performance, we solve 9 to 11 equations of Eq. (1) in the basis set size of $N=200-850$ and investigate the error dependence of Hamiltonian eigenenergies and complex resonance energies on N and CPU times for *SIN* and *LOB*, respectively. Two sets of results with moderate accuracy (i.e., with the error <0.1 cm⁻¹) appear perfectly superimposed as shown in Fig. 1.

The characteristics of Hamiltonian eigenenergy (ε) error

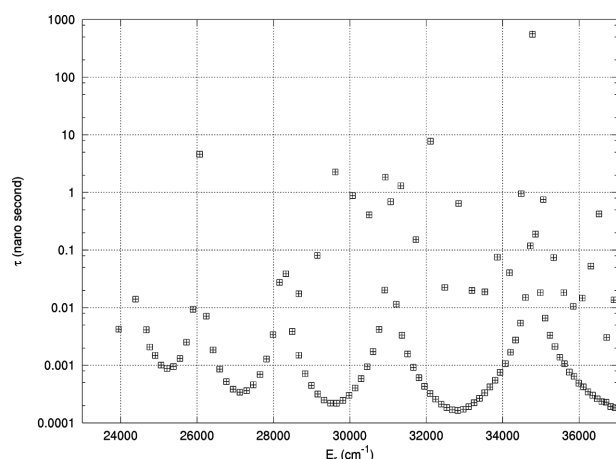


Fig. 1. E_s presented as E_r vs τ . The pluses (+) and boxes (□) denote the results of using SIN ($N=240$, $v=X$, quadrature rule= B) and LOB ($N=370$, $v=F$, quadrature rule= B), respectively. The largest difference between two calculated E_s 's is 0.0859 cm^{-1} in E_r .

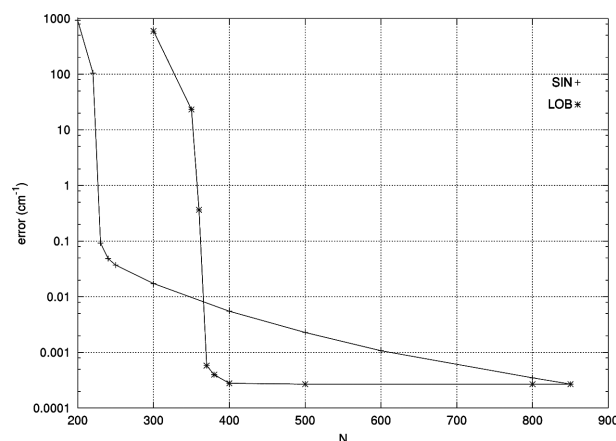


Fig. 2. Hamiltonian eigenenergy error vs basis set size. The largest errors are presented. The error is calculated as $|\varepsilon_i - \varepsilon_i^{ref}|$ for 139 initial guesses (ε_i) of resonance energies where the reference energy ε_i^{ref} are eigenenergies obtained for the bound-type Hamiltonian using $N=850$ and serves as the reference for error calculations. In this way, both error curves converge to identical value at $N=850$ whose value indicates the degree of mutual convergence of SIN and LOB . They may reflect the errors to unknown exact values because they are obtained from two totally independent kinds of basis functions.

convergence behavior of LOB and SIN are presented in Fig. 2. Each error curve shows rapid convergence followed by slow convergence portion. The onset of rapid converging portion corresponds to the local basis set density value of one basis point per half of local wavelength at the asymptotic potential energy curve region for ϕ_1 channel wave at $37,000 \text{ cm}^{-1}$. Meanwhile, the slow converging region extends to larger basis set density region beyond this threshold region. The SIN case requires less number

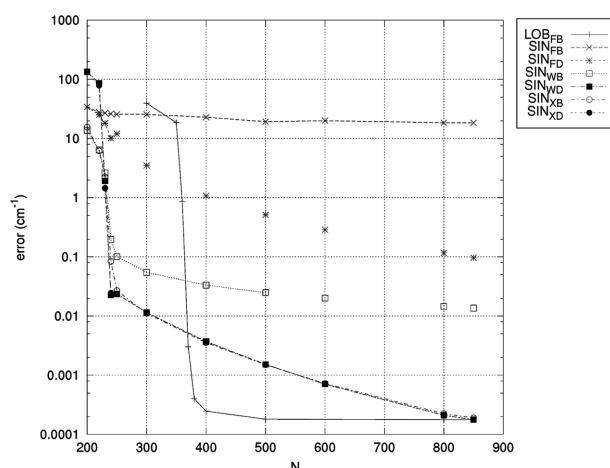


Fig. 3. The largest resonance energy error vs basis set size. Error curves are presented for LOB ($v=F$ and quadrature rule= B), and SIN ($v=F, W, X$ and quadrature rule= B, D), respectively. The error is calculated as $|E_s - E_s^{ref}|$ for 112 resonance energies in a similar manner as in Fig. 2. The results of LOB_{FB} using $N=850$ (CPU time=2469 sec) serve as the reference for the error calculation of SIN case, while those of ($N=850$, CPU time=2970 sec) do for LOB_{FB} . Note that SIN_{WD} and SIN_{XD} results appear perfectly superimposed and that for smaller N 's, some resonance states are failed to be calculated.

of basis functions than LOB case to achieve the error less than 0.1 cm^{-1} . It is readily noticed that the SIN and LOB converges with quite different rates, moreover LOB achieves saturated values earlier than SIN . Further discussion follows later.

Resonance energy error convergence behavior is presented in Fig. 3. Since, for LOB case, essentially identical results are obtained regardless of the choice of v and integration methods, we choose " F and B " case which requires the most CPU time saving calculation. On the other hand, for SIN case, the results are substantially varying depending on those choices. The most accurate results are obtained when quadrature rules D and boundary function X are used, which also requires the largest CPU times.

To investigate the effect of the boundary function choice for SIN case, we use quadrature rules D to exclude any possibility of inaccurate integrations. The errors decrease rapidly beyond the threshold basis set density for W and X but relatively slowly for the choice of F . This difference results from the fact that the boundary functions W and X account for a large fraction of the resonance wavefunction in the asymptotic region, and consequently, alleviate the work of the basis set in representing the wavefunction, which is not the case of F .

Meanwhile, the effects of integration methods are quite different depending on the boundary function choice. For

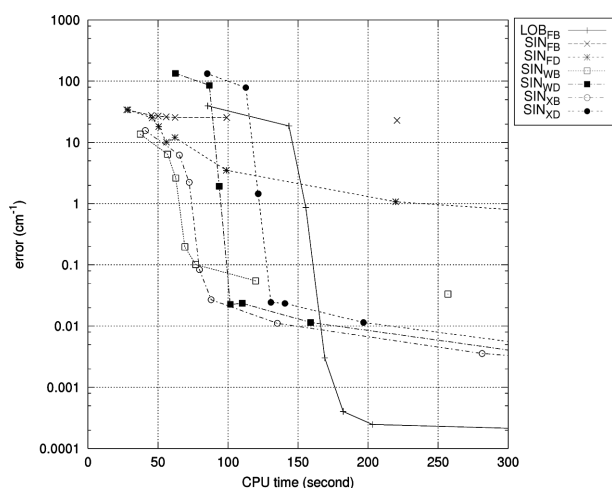


Fig. 4. The largest resonance energy error vs CPU times. See the figure caption of Fig. 3 for the legend.

F and W , the errors improve a lot by changing the quadrature rules from B to D . However, the improvement is almost null for X . This observation can be rationalized by noting the behavior of the integrand $(H+L-E_s)|v\rangle$ near the outer boundary. Since this function does not vanish for $v=F$ or $v=W$, the corresponding integral cannot be accurately evaluated by B because these quadratures are based on one-dimensional box eigenfunctions vanishing at both ends. On the contrary, the integrand vanishes almost for $v=X$, therefore, substantial accuracy was already achieved by the quadrature rules B . In fact, we may use the numerically calculated E_s to define v and repeat solving Eq. (1) to find the refined E_s until exact convergence is achieved. However, actual calculation shows that X is the best in terms of calculation costs and accuracy improvements.

The CPU time requirements are presented in Fig. 4 obtained using a general PC. Considering Fig. 3 also, it is seen that SIN with X and B is the most efficient for moderately accurate results, i.e., below error of 0.1 cm^{-1} at about 80 sec corresponding to basis set size of $N=240$. Note also that SIN with W and B nearby shows almost comparable accuracy. However, LOB surpasses SIN at about 160 sec corresponding to $N=370$ where the error is far less at about 0.01 cm^{-1} .

DISCUSSION

Finally, we discuss the reason behind the relatively slow convergence rate of SIN compared to LOB as N increases. Since SIN basis set density is lower than LOB near both boundary regions, we conjecture that SIN is not appropriate for those regions. Therefore, we artificially truncate the potential couplings $V_{ij(i \neq j)}$ near both ends and making the dissociative V_{11} reaches constant value earlier asymptotically. Then, it is seen that the bound-type Hamiltonian eigenfunctions of lower energies are warded off from the potentially forbidden region (near the inner boundary) and, also, accurately represented near the asymptotic region (outer boundary) because SIN is already eigenfunctions of constant potential Hamiltonian. In other words, we artificially make the SIN more appropriate basis for the Hamiltonian. Indeed, both the eigenenergy and resonance energy convergence rates of SIN become comparable to LOB for this artificial Hamiltonian. Therefore, the slow convergence is not inherent in the SIN basis but caused by the somewhat inappropriate combination of calculation parameters for the present resonance system.

In short, *the SIN achieves the same moderate accuracy with about two thirds of basis set size and one half of CPU times than the LOB for the present problem* as can be seen from Figs. 3 and 4, which is the main conclusion of this work.

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