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Detection and analysis of interloping molecular resonances

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An analytic method that exploits the properties of the eigenphase sum and its derivative is developed and implemented to study resonance structure found in the phase shift for electron scattering by diatomic molecular cations. The approach is used to locate narrow resonances and identify interloper resonances found within dominant Rydberg series. The power of the technique is illustrated for two molecular cations (oxygen and titanium oxide). [S1050-2947(99)50412-5]

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The vast majority of theoretical methods used to detect resonances invariably involve some form of fitting procedure with all its inherent difficulties and limitations [1,2]. Recent success using the eigenphase sum derivative to analyze resonances found in *ab initio* R-matrix studies of electron interactions with atomic ions has been demonstrated [3,4] when compared to experimental and theoretical results. Similarly, work performed recently on ultracold–atom-molecule (He-H_2) collisions employed an approach based on using the numerical derivative of the eigenphase sum on an fine energy mesh to analyze narrow isolated Feshbach resonances [5]. The eigenphase sum in He-H_2 collisions was obtained via a rovibrational close-coupling approach [6]. The generality of the present approach would make it feasible to determine similar properties of narrow resonances found in ultracold–atom-molecule or atom-atom collision complexes, provided an R-matrix description of the collision complex exists, as in the case of reactive scattering from atom-diatom complexes [12]. Interloper resonances are important to understand as their presence disrupts the regular Rydberg resonance series pattern, whereas those straddling thresholds will clearly enhance reactive rates. The widths of the interloping resonances are in general broader than those belonging to the dominant Rydberg series in their vicinity due to their larger binding energies [6]. Presently, this elegant and widely applicable approach is adapted for use both within a multistate configuration interaction and a multichannel context to study quasibound interloping narrow resonances found in electron molecular-ion collision complexes.

Our method is based on the analysis of the eigenphase sum derivative to interpret interloping resonances found within a dominant Rydberg series. The present approach relies on the R matrix being an analytic function of energy and therefore differentiable to provide the derivative of the eigenphase sum in scattering collisions [3,4]. Resonant states of TiO are of importance in cool stars [7] and information on resonant states of molecular oxygen (O_2) are currently of interest in photoabsorption measurements [8]. Reliable techniques are clearly desirable for the analysis of such resonances series, a problem that the present method addresses. Therefore, $O_2{}^+$ and the heteronuclear TiO^+ ion are chosen to illustrate the applicability of the method. An alternative method (the time delay of the S matrix), first applied by Smith [9] in low-energy heavy-particle collisions, has recently been implemented for the case of electron scattering from molecules, comparing favorably with the standard Breit-Wigner approach [10,11].

In the study of electrons colliding with molecules, R-matrix theory partitions Hilbert space into two regions. The inner region is defined by a hypersphere of radius a centered on the center of mass of the complex, chosen to effectively enclose the target electrons' charge cloud [13]. When the incident electron is within this hypersphere, a multicenter expansion is used to solve the many-body Schrödinger equation. Outside of this hypersphere, the neglect of electron exchange in the molecular system reduces the complexity of the collision problem and the R matrix connects the two regions.

The reactance matrix (**K**) and the associated **T** or **S** matrix determined in electron molecule collisions contain the information on the scattering process, from which one may calculate the relevant physical observables. The power of the R-matrix approach is the fact that the solution of a system of coupled equations is replaced by a single matrix diagonalization. This is of great practical importance in the region of narrow resonances where solutions are needed for many closely spaced electron-impact energies to fully resolve the structure.

In multistate close-coupling electron molecule collisions for certain collision energies and scattering symmetries, structure (identified as Feshbach Rydberg resonances) is seen in the eigenphase sum approaching the thresholds of the excited states of the target cation. A resonance manifests itself in theoretical calculations by a rapid increase of π radians in the total eigenphase sum superimposed on a background. In practice, because a resonance has a finite width, the increase in the eigenphase sum may not be exactly π due to the background variation. Therefore, a more useful definition of a resonance position is the energy at which the gradient of the eigenphase sum is maximum, i.e., the derivative $d\delta/dE$. The energy positions of Rydberg resonances are seen to obey the formula $\epsilon_\infty - \epsilon_{nl\lambda} = z^2/(n-\mu_{nl\lambda})^2 = z^2/\nu^2$ where ν is the effective quantum number, n the principal quantum number, l the orbital angular momentum number, λ the projection of l

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along the internuclear axis, and where $\mu_{nl\lambda}$ is the quantum defect. Rydberg states of the molecule can then be assigned as $^{(2S+1)}\Lambda{:}nl\lambda$, with S being the total spin and Λ the total orbital angular-momentum projection along the internuclear axis, which echoes Rydberg's empirical formula for term series in the spectra of alkali-metal atoms; $T_n = T_\infty - RZ^2/(n-\mu_n)^2$ [19].

Qualitatively the need for a quantum defect arises from the fact that, as the electron penetrates the molecular cloud, it no longer recognizes the target as a point charge and compensates for the deviation away from a pure Coulombic field. The incident electron and molecular charge cloud can interact in a way similar to a simple hydrogenic system. Core-excited resonances may arise from the fact that the incident electron energy is not sufficiently large enough to escape initially, and that after excitation the electron loses sufficient energy to coincide with one of the quasi-bound-state energies allowed in the field produced by the excited target molecule. The electron then requires time to regain the effective binding energy $\epsilon_{nl\lambda} = z^2/(n-\mu_{nl\lambda})^2 = z^2/\nu^2$ to escape from the target. The quantum defect $\mu_{nl\lambda}$ is dependent on the orbital angular momentum *l*, and to lesser extent on whether the incident electron is $\sigma, \pi, \delta, \ldots$, in character. As the orbital angular momentum *l* increases, core penetration diminishes and the effective quantum number ν becomes more integer-like and can be interpreted as the bound Rydberg electron being compelled to occupy distant orbitals outside the core.

When considering *m* overlapping and interacting resonances with a background phase, the most established way of analyzing resonances is by superimposing the Breit-Wigner form onto an eigenphase sum $\delta(E)$ given by

$$\delta(E) = \delta_0(E) + \sum_{i=1}^{m} \tan^{-1}\frac{\Gamma_i}{2(E_r^i - E)}.$$

Here $\delta_0(E)$ is the slowly varying background phase (normally linear or quadratic in energy) and Γ_i and E_r^i are respectively the width and energy position of the ith resonances.

The present method exploits the analytical properties of the *R* matrix to obtain the energy derivative of the reactance (**K**) matrix, without using a pure Coulomb potential at a large scattering distance. The method defines matrices **Q** and **B** in terms of asymptotic solutions (hence its name), the *R* matrix and the energy derivatives, so that $d\mathbf{K}/dE = \mathbf{B}^{-1}\mathbf{Q}$, from which eigenphase gradients of the **K** matrix are obtained. Resonance positions are then defined as the maximum gradient, with their associated widths being related to the inverse of the eigenphase gradients. The *QB* technique is centered around diagonalizing the **K** matrix in the external region to provide an eigenphase sum from which the derivative allows the determination of the relevant resonance parameters. The *ab initio* quantum chemistry approach for electron-molecule collisions [14] provides the inner-region surface amplitudes (w_{ij}) and eigenenergies (poles ε_j) from Wigner-Eisenbud *R*-matrix theory [14–17], together with the necessary Buttle [18] corrections. The solution of the electron-molecule scattering problem provides the reactance (**K**) matrix and the appropriate eigenphase sum $\delta(E)$.

TABLE I. Comparison of experimental and theoretical ionization energies and effective quantum number ν for the $[b\ ^4\Sigma_g^-]$ $np\pi_u$ quasibound Rydberg states of molecular oxygen in the $^3\Pi_u$ symmetry, with our five state work at the internuclear separation of $2.3a_0$. Δ_1, Δ_2, and Δ_2 are percentage differences.

	E (Ry)[a]			ν				
$np\pi_u$	QB	CLL[b]	Δ_1[d]	QB	CLL[b]	YT[c]	Δ_2[e]	Δ_3[f]
$3p\pi_u$	−0.184	−0.205	11.4	2.335	2.247		3.8	
$4p\pi_u$	−0.090	−0.095	5.6	3.340	3.283	3.313	1.7	0.8
$5p\pi_u$	−0.053	−0.055	3.8	4.336	4.287	4.333	1.1	0.1
$6p\pi_u$	−0.035	−0.036	2.9	5.322	5.273	5.335	0.9	0.2
$7p\pi_u$	−0.025	−0.026	4.0	6.302	6.246	6.325	0.9	0.4
$8p\pi_u$	−0.019	−0.018	5.3	7.257	7.209	7.326	0.7	1.0

[a] Ionization energy (Ry) relative to the $b\ ^4\Sigma_g^-$ cation state.
[b] Theoretical values from Chung, Lin, and Lee [20].
[c] Experimental values from Yoshino and Tanaka [21].
[d] Δ_1 for resonance positions with Ref. [20].
[e] Δ_2 for effective quantum number ν with Ref. [20].
[f] Δ_3 for effective quantum number ν with Ref. [21].

Following the work of Berrington and co-workers [3,4] to locate the resonances, we find the maxima in the eigenphase sum derivative. Resonance widths Γ are related to the inverse of the eigenphase sum derivative at resonance, as can be seen by differentiating the Breit-Wigner form and assuming the background gradient $\overline{\delta'} \ll \Gamma^{-1}$, and setting $E = E_r$ one gets

$$\Gamma = 2/\delta'(E_r). \tag{1}$$

Generalizing to the multichannel case (channel *i*), the normalized widths Γ_i are obtained by projecting onto the open channels using the *K*-matrix eigenvectors **X**, which are related to the autoionization decay rates by $\Gamma_i/\Gamma = \Sigma_{j=1}^{n_0} X_{ij}\delta_j'/\delta'$, where n_0 is the number of open channels [4]. Since the Breit-Wigner form is valid strictly for isolated resonances, one should estimate the perturbation of the width by a nearby resonance [3]. Differentiating the Breit-Wigner form and evaluating at $E = E_r$ gives the expression

$$\delta'(E_r) = \overline{\delta'}(E_r) + 2/\Gamma \Rightarrow \Gamma = 2/[\delta'(E_r) - \overline{\delta'}(E_r)], \tag{2}$$

which includes the effect of a background gradient.

To illustrate the applicability of our method to electron–molecular-ion collisions, the $^3\Pi_u$ scattering symmetry for the e^--$O_2{}^+$ homonuclear complex and the $^3\Delta$ symmetry for the e^--TiO$^+$ heteronuclear system are considered respectively in five- and three-state close-coupling approximations. A valence configuration-interaction representation is used for both the target and scattering molecular wave functions within the context of the *R*-matrix *ab initio* approach. The diagonalization of the appropriate electronic Hamiltonian with the Bloch operator ensures Hermiticity and yields the appropriate surface amplitudes (w_{ij}) and eigenenergies (poles ε_j), which are the starting points for the outer region solutions of the coupled differential equations. In *ab initio* *R*-matrix studies of electrons colliding with molecules, a boundary radius of $10a_0$ is normally chosen that ensures that the target charge cloud density is totally enveloped within this hypersphere. This inner region is enlarged so that the potential matrix elements coupling the target states V_{ij} at and

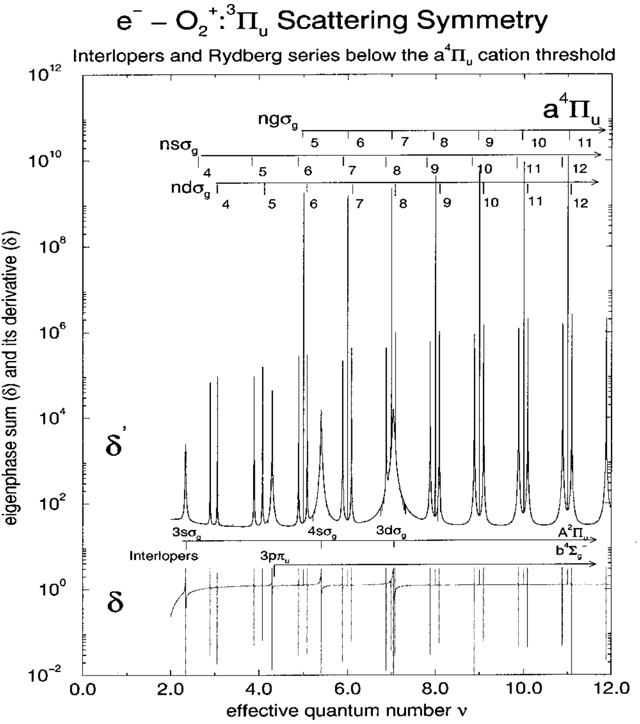

FIG. 1. Eigenphase sum and its derivative as a function of effective quantum number ν for the ${}^3\Pi_u$ scattering symmetry of e^--O_2^+, below the lowest-lying $a\ {}^4\Pi_u$ threshold at the fixed bond separation of 2.3 Bohr. The $ns\sigma_g$, $nd\sigma_g$, and $ng\sigma_g$ series converging to the $a\ {}^4\Pi_u$ threshold are identified, as are the interlopers $3s\sigma_g$, $4s\sigma_g$, and $3d\sigma_g$ associated with the $A\ {}^2\Pi_u$ and the $3p\pi_u$ with the $b\ {}^4\Sigma_g^-$ thresholds.

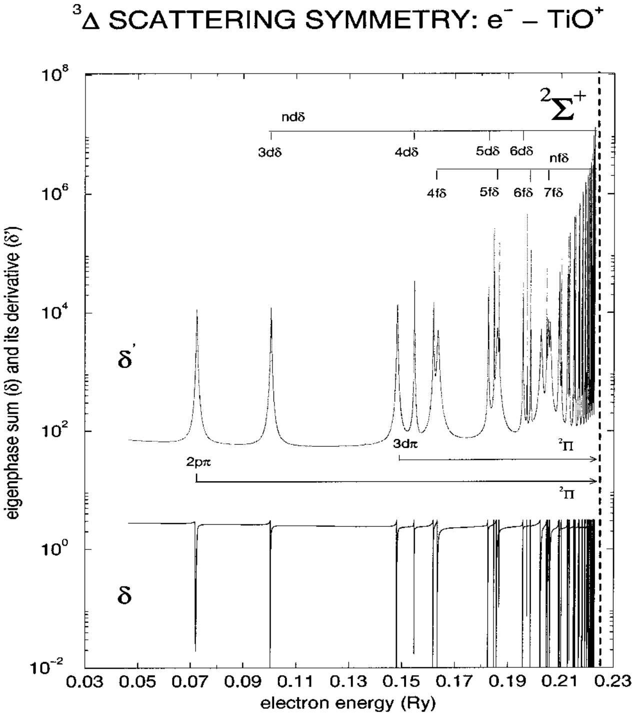

FIG. 2. Eigenphase sum and its derivative as a function of collision energy for the ${}^3\Delta$ scattering symmetry of e^--TiO$^+$, below the lowest-lying ${}^2\Sigma^+$ threshold at the fixed bond separation of 2.9 Bohr. The $nd\delta$ and and $nf\delta$ series are identified, as are the two interlopers $2p\pi$ and $3d\pi$ associated with the higher-lying $1\ {}^2\Pi$ threshold.

beyond the hypersphere may be set to zero, which simplifies the collision problem in the outer region. The validity of this approximation is dependent on the diatomic cation, the magnitude of the appropriate dipole and quadrupole moments, the associated potential coupling coefficients, and the arbitrary choice of the *R*-matrix boundary size. In the case of the e^--O$_2^+$ complex, a radius of $15a_0$ was used, and for e^--TiO$^+$ collisions it was increased to $18a_0$. Investigation of the coupling potential matrix elements between states for these systems, at and beyond the hypersphere radius, indicated that they were $\approx 10^{-6}$ and 10^{-5}, respectively, which justifies their neglect.

Table I presents our results from the *QB* method for the ${}^3\Pi_u$ scattering symmetry in e^--O$_2^+$ collisions. Our results when compared with previous theoretical [20] and experimental studies [21] for the effective quantum numbers of the $np\pi_u$ Rydberg series approaching the $b\ {}^4\Sigma_g^-$ threshold of the O$_2^+$ cation show excellent agreement. The position of the lowest resonance shows the greatest variation between the methods, as it is likely to be the most sensitive to the collision model. The derivative of the eigenphase sum of an unperturbed series would follow a ν^3 law, whereas the presence of interlopers are seen visually to break that pattern in Figs. 1 and 2. Figure 1 compares the eigenphase sum and its derivative as a function of effective quantum number ν for the ${}^3\Pi_u$ scattering symmetry in e^--O$_2^+$ obtained using the *QB* method. Interloping resonances are clearly distinguishable in the derivative of the eigenphase sum and the $ns\sigma_g, nd\sigma_g, ng\sigma_g\ a\ {}^4\Pi_u$ Rydberg series identified. For the O$_2^+$ cation the most self-evident are typically broader, as they are either the first/second member of higher-lying series that usually interlopes with Rydberg members ($n \geqslant 5$) associated with the lower-lying thresholds. This may not always be the case, as it depends on the compactness of the target cation excited-state thresholds. In general, the derivative of the eigenphase sum of the interlopers stands out in stark contrast to that of the expected Rydberg series.

Table II gives the total and partial decay widths for two members of the $ns\sigma_g$ and $nd\sigma_g$ series converging to the $a\ {}^4\Pi_u$ threshold of the O$_2^+$ cation. Results from Table II indicate that for the $4s\sigma_g$ and $5s\sigma_g$ resonances, ≈40% of

TABLE II. Total and partial autoionization decay resonances widths (units of Rydbergs) and effective quantum numbers ν for two members of the $ns\sigma_g, nd\sigma_g$ series converging to the $a\ {}^4\Pi_u$ threshold and the $3s\sigma_g$ interloper associated with the higher-lying $A\ {}^2\Pi_u$ threshold found in the ${}^3\Pi_u$ scattering symmetry of the e^--O$_2^+$ collision complex at $2.3a_0$.

Resonance state	ν	Total (Ry) Γ	$\Gamma_{l=1}$	Partials (Ry) $\Gamma_{l=3}$	$\Gamma_{l=5}$
$3s\sigma_g\ A\ {}^2\Pi_u$	2.3377	8.004^{-4}	7.148^{-4}	0.832^{-4}	0.024^{-4}
$4s\sigma_g\ a\ {}^4\Pi_u$	2.8955	2.907^{-5}	1.244^{-5}	1.663^{-5}	0.0
$5s\sigma_g\ a\ {}^4\Pi_u$	3.8869	2.123^{-5}	9.808^{-6}	1.140^{-5}	0.0
$4d\sigma_g\ a\ {}^4\Pi_u$	3.0591	2.143^{-5}	1.290^{-5}	8.508^{-6}	0.0
$5dgj_g\ a\ {}^4\Pi_u$	4.0758	1.273^{-5}	8.313^{-6}	4.417^{-6}	0.0

the total width decays to the channel with angular momentum $l=1$, whereas ≈60% decays to the channel with $l=3$ coupled to the ground-state cation. The reverse occurs for the $4d\sigma_g$ and $5d\sigma_g$ resonances. In the case of the $3s\sigma_g$ interloper the decay is primarily (≈90%) into the channel with angular momentum $l=1$. The power of the QB technique is the ability to detect interloping resonances and to analyze narrow resonances, providing information on partial and total autoionization widths, as the conventional method of fitting the Breit-Wigner form to the eigenphase sum becomes numerically unstable when autoionization widths are less than $\approx 10^{-6}$ Ry. For TiO^+, Fig. 2 presents the eigenphase sum and its derivative for the energy region below the $^2\Sigma^+$ threshold. Two interlopers are present, $2p\pi$ and $3d\pi$, associated with the higher-lying $1\ ^2\Pi$ threshold and interspersed in the regular $nd\delta$ and $nf\delta$ Rydberg series. The $ng\delta$ series, although present, have not been analyzed.

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