The Complex Coordinate Rotation Method and Exterior Scaling: A Simple Example

JACK SIMONS[*]
Chemistry Department, University of Utah, Salt Lake City, Utah 84112, U.S.A.

Abstract

The so-called complex coordinate rotation technique is applied to two simple one-dimensional piecewise-defined model potentials. The invariance of the bound and resonance energy levels of these potentials under coordinate rotation is analyzed. It is shown that a proper treatment of the coordinate rotation gives a natural and easily understood introduction of the so-called exterior scaling. Implications for application of the coordinate rotation method to physically reasonable electron–atom or electron–molecule potentials are also discussed. Finally, the relative merits of the rotation procedure and the direct Siegert search method proposed by Miller et al. are evaluated.

1. Introduction

Several years ago, it was demonstrated by Aguilar and Combes [1], Balslev and Combes [2], and Simon [3] that certain (dilatation analytic) electronic Hamiltonians $H(r)$ could be continued analytically by replacing each electronic coordinate r_j by a "scaled" coordinate[†] $r_j \exp(i\alpha)$. The resultant scaled Hamiltonian $H_\alpha(r)$ [which, for example for an atom[‡] of charge Z, is $\exp(-2i\alpha)\,\Sigma_{j=1}^{Z} -\frac{1}{2}\nabla_j^2 - Z\exp(-i\alpha)\,\Sigma_{j=1}^{Z} r_j^{-1} + \exp(-i\alpha)\Sigma_{i\neq j}^{z}\gamma_{ij}^{-1}$] was shown by the above authors to possess the same bound energy levels (but not the same wavefunctions) as the original $H(r)$. They also demonstrated that the resonances of $H(r)$, which are discussed in more detail below, occur as complex energy levels[§] [$E = \epsilon \exp(-i\beta)$] of H_α whose corresponding wavefunctions are square integrable provided that the so-called "coordinate rotation angle" α is greater than one-half the magnitude of the complex energy's phase β. These facts lead many researchers [4–10] to explore the exciting possibility that these resonance wavefunctions, which are not square-integrable eigenfunctions of $H(r)$, could be found by using conventional (square-integrable Gaussian or Slater) basis function techniques.

---

[*] Camille and Henry Dreyfus Foundation Fellow, John Simon Guggenheim Fellow.

[†] All electronic coordinates are scaled by the same amount because of the indistinguishability of the electrons.

[‡] For a diatomic molecule, the nuclear attraction part of the electronic Hamiltonian scales as

$$-Z_A \sum_{j=1}^{Z_A+Z_B} |r_j \exp(i\alpha) - R_A|^{-1} - Z_B \sum_{j=1}^{Z_A+Z_B} |r_j \exp(i\alpha) - R_B|^{-1}$$

which is not a simple homogeneous function of r.

[§] Such a complex energy, when substituted into $\psi(x,t) = \psi(X)\exp(-iEt)$, gives an exponentially decaying time dependence to $|\psi|^2$ with a lifetime $\tau = (2\epsilon \sin\beta)^{-1}$.

International Journal of Quantum Chemistry: Quantum Chemistry Symposium 14, 113–121 (1980)
0161-3642/80/0014-0113$01.00

A great deal of computational information was recently generated by applying the coordinate rotation technique (CRT) to electron–atom and electron–molecule resonances which use model one-electron potentials [6a], configuration interaction wavefunctions [5c,6b], explicitly correlated wavefunctions [5b,5e,8j,8k], static exchange potentials [5a], or many-body Green's function methods [9]. It is the primary purpose of this article to present (in Sec. 2) a clear explanation of how the CRT applies to a few simple one-dimensional model problems and to point out some of the potentially confusing aspects of its use, and show its connection with exterior scaling theory [11]. The implications which observations derived from these model problems have for physically realistic electron–atom and electron–molecule scattering studies are also brought to light in Sec. 3.

2. Coordinate Rotation Applied to Piecewise Potentials

To motivate physically the introduction of the coordinate rotation transformation, we consider the motion of an "electron" in the one-dimensional potential defined by $[v(x) = 0, 0 \leqslant x \leqslant L;\ v(x) = V, L < x < \infty]$. Such a potential might be thought of as representing the electron–atom radial potential for s-wave ($l = 0$) scattering. The unrotated Schrödinger equation

$$-\frac{1}{2}\frac{d^2}{dx^2}\psi + v(x)\,\psi = E\psi, \quad \psi(0) = 0 \tag{1}$$

has bound states ($E < V$) which obey $\psi(x \to \infty) = 0$. The energy levels of the bound states arise from matching $[(d\psi/dx)/\psi]$ at $x = L$, where $\psi(x) = A \sin(kx)$, $0 \leqslant x \leqslant L$; $\psi(x) = C \exp(-Jx)$, $L \leqslant x < \infty$; and $k \equiv \sqrt{2E}$, $J = (2v - k^2)^{1/2}$. The resulting equation which can be used to solve for the bound energy levels is $\tan(kL) = -k/J$, which can easily be solved graphically or numerically for the *real* bound energy levels. The continuum ($E > V$) wavefunctions of the above Hamiltonian are given by $\psi(x) = A \sin(kx)$, $0 \leqslant x \leqslant L$; $\psi(x) = B \exp(i\bar{J}x) + C \exp(-i\bar{J}x)$, $L \leqslant x < \infty$ with $\bar{J} = (k^2 - 2V)^{1/2}$. Of course, the amplitudes C and B can be related to A via the two equations stating the continuity of ψ and $d\psi/dx$ at $x = L$. Thus far, the above discussion is nothing but a treatment of the usual textbook-level problem.

Siegert showed [12] in 1939 that one could find continuum solutions to the above problem which have continuous $\psi(x)$ and $d\psi/dx$ but which also possess no incoming flux ($C = 0$). In this classic article, Siegert demonstrated that the imposition of this extra constraint ($C = 0$) could only be realized if the Schrödinger equation energy E assumed complex values. For the above-specified problem, the imposition of $C = 0$ leads to $\tan(kL) = -ik/\bar{J}$ which is to be solved for the complex energy levels. The solution of this complex transcendental equation is treated in the Appendix. Siegert also showed how these complex energies $E = E_r - i\Gamma/2 \equiv \epsilon \exp(-i\beta)$ were related to the scattering resonance energies (E_r) and widths (Γ) which could also be obtained from a more conventional phase-shift energy-dependence study.

However, when one looks carefully at the nature of the Siegert resonance wavefunction for large x, one finds that $\psi(x)$ is exponentially diverging since $D \exp(ikx) = D \exp[ix\sqrt{2\epsilon}\cos(\beta/2) + \sqrt{2\epsilon}\, x \sin(\beta/2)]$ and, as is shown in the Appendix and by Siegert, $\beta > 0$. This divergence could be circumvented if the "electronic coordinate" x were allowed to assume complex values [$x = y \exp(i\alpha)$], for then $D \exp(ikx) = D \exp[iy\sqrt{2\epsilon}\cos(\alpha - \beta/2) - y\sqrt{2\epsilon}\sin(\alpha - \beta/2)]$ which is square integrable as long as $\alpha > \beta/2$. Of course, it is not *physically* meaningful to consider complex values of x. However, if one could show that, by mathematically permitting x to assume complex values, the desired resonance *energy levels* of the modified [by $x = y \exp(i\alpha)$] problem were unchanged, then a very interesting possibility immediately presents itself. By coordinate rotating x [$x = y \exp(i\alpha)$], one should be able to find the resonance energy levels by using square-integrable approximations for the eigenfunctions of the rotated problem. It is the author's opinion that the extension of Siegert's original idea [12] to permit rotated "electronic" coordinates provides a physically clear motivation for introducing the CRT. The mathematically rigorous justification of the CRT theory has been provided in refs. 1–3, where it is shown that both the resonance (if $\alpha > \beta/2$) and bound eigenenergies are unchanged by the rotation and that both kinds of eigenstate possess square-integrable wavefunctions.

To better understand how certain energy levels (bound and resonance) of $H_\alpha(r)$ can be identical to those of $H(r)$, let us return to the above "square-well" potential problem. The rotated Schrödinger equation $-\frac{1}{2}\exp(-2i\alpha)(d^2/dy^2)\psi = (E - V)\psi$, $\psi(0) = 0$, has (for $\mathrm{Re}\, E < V$) solutions $\psi(y) = A \sin[ky \exp(i\alpha)]$, $\psi(y) = D \exp[J \exp(i\alpha) y] + C \exp[-J \exp(i\alpha) y]$, where k and J are as defined above except that E is now thought of as complex. To obtain the "allowed" energy levels for $\mathrm{Re}\, E < V$, one must insist that $(d\psi/dy)\psi$ be continuous at $y = L \exp(-i\alpha)$, *not* at $y = L$. That is, in the *interior* ($x \le L$) region, the coordinate rotation is nothing but a trivial redefinition of variables; the boundary conditions on ψ are unchanged! This constraint leads to $\tan(kL) = -k/J$, which is identical to the "energy level equation" for the bound states of the unrotated problem. Of course, in the *exterior* region ($|x| = |y| > L$) the "rotation" does change the behavior of $\psi(y)$ since $\psi(y)$ is now square integrable. This idea of scaling only the asymptotic part of the problem has been called "exterior scaling" [11].

The Siegert resonance states belonging to the above potential should also be invariant to rotation. By matching the logarithmic derivative of $A \sin[k \exp(i\alpha) y]$ to that of $D \exp[iJy \exp(i\alpha)] + C \exp[-iJy \exp(i\alpha)]$ at $y = L \exp(-i\alpha)$ *not* at $y = L$, one obtains exactly the same equations as resulted in the unrotated problem. Then, by enforcing $C = 0$, one obtains exactly the same Siegert resonance condition. Thus, the resonances are indeed unchanged. The nonresonant scattering solutions to the rotated Schrödinger equation, $A \sin[ky \exp(i\alpha)]$ and $D \exp[iJy \exp(i\alpha)] + C \exp[-iJy \exp(i\alpha)]$, do not have their energies specified by a condition like $C = 0$. Their energies are not quantized and are simply the unrotated energies times $\exp(-2i\alpha)$. That is, the rotated Schrödinger equation has a continuum eigenfunction of the unrotated Schrödinger equation having energy E.

The lesson which is learned from the above simple example is that the process of using the exterior scaled coordinate rotation does not alter the *nonasymptotic* boundary conditions which ψ must obey. ψ and ψ' are still continuous at the real *physical* point $x = L$, which corresponds to the *mathematical* rotated point $y = L \exp(-i\alpha)$. The process of rotation does change the asymptotic spatial behavior (in y space) by making $\psi \to 0$ as $y \to \infty$. This mathematical consequence then permits one to expand $\psi(y)$ in square-integrable functions of y as a device for finding the bound and resonance energies.

Next we consider a potential $[V(x) = 0, 0 \leqslant x \leqslant L; V(x) = V, L \leqslant x \leqslant L + T; V(x) = 0, L + T < x < \infty]$ which can be thought of as crudely representing the radial potential for p-wave ($l = 1$) electron–atom scattering. Such a potential supports no bound states but it does have true shape resonances in contrast to the first potential considered which has only "virtual states" since it has no "angular momentum barrier." The unrotated Schrödinger equation for the above potential (for Re $E < V$) has solutions $\psi = A \sin(kx)$, $0 \leqslant x \leqslant L$; $\psi = C \exp(-Jx) + D \exp(Jx)$, $L \leqslant x \leqslant L + T$; $\psi = F \exp(ikx) + G \exp(-ikx)$, $L + T \leqslant x < \infty$. Applying the continuity condition to ψ and ψ' at $x = L$ and $x = L + T$ permits one to solve for G in terms of F. By then, as Siegert suggests [12], insisting that ψ possess no incoming flux ($G = 0$), one obtains the following "resonance energy condition":

$$\tan(kL) \times k/J = -\exp(-2JT)(1 + J/ik)(1 - J/ik)^{-1} [\tan(kL) - (k/J)] \quad (2)$$

To gain some insight into the nature of the (resonance) solutions of this equation, let us consider the case of a thick (T large) barrier with Re $E \ll V$ (so that Re J is large). In this case, we expect the resonance to be quite sharp (Im E small). We can now solve for the resonance energy by "iterating" the above equation. First, we ignore the entire right-hand side of this equation since $\exp(-2JT) \approx 0$. The resulting condition, $\tan(kL) = -k/J$, is identical to the bound-state energy condition resulting from the model potential considered earlier. This is not surprising for such a thick, high barrier.

With the solutions to $\tan(kL) = -k/J$ taken as "zero-order" solutions to the full-resonance energy equation given above, we can obtain an improved estimate of the true solutions. We simply use the (real) zero-order energies (call them k_0, J_0) to evaluate the right-hand side of the full equation. In the left-hand side, we replace k by $k_0 + \delta$ [and $J = (2V - k^2)^{1/2}$ by $J = (2V - k_0^2 - 2k_0\delta - \delta^2)^{1/2}$] and expand $\tan(kL)$ and k/J in powers of the "correction" δ, keeping terms through first order in δ. The resulting equations can easily be solved for δ, giving $L\delta = [2k_0/J_0 \exp(-2J_0T)(1 + J_0^2/k_0^2)^{-1} (1 - J_0^2/k_0^2 - 2iJ_0/k_0)][1 + \tan^2(k_0L) + (J_0L)^{-1} + k_0^2/J_0^3L]^{-1}$. This correction to the (real) k_0 yields an "improved" value of k which, as Siegert shows, has a negative imaginary part. The imaginary component of δ gives [through $E = \frac{1}{2} k^2 = \frac{1}{2} (k_0^2 + 2k_0\delta + \delta^2)$] the width ($\Gamma$) of the resonance ($E = E_r - i\Gamma/2$) as $\Gamma = (8k_0/L) \exp(-2J_0T)(1 + J_0^2/k_0^2)^{-1} [1 + \tan^2(k_0L) + (J_0L)^{-1} + k_0^2/J_0^3L]^{-1}$. This result for Γ is physically quite resonable. It contains the exponential damping factor $\exp(-2J_0T)$, and as the resonance energies (k_0^2) increase relative to V, the resonance widths Γ also increase. These observations are not at all surprising.

The exterior-scaled coordinate-rotated version of the above Schrödinger equation has solutions which, upon applying the continuity equations at $y = L \exp(-i\alpha)$ and $y = (L + T) \exp(-i\alpha)$ and imposing $G = 0$, yield exactly the same resonance energy condition as was analyzed above. The only advantage to solving the coordinate-rotated Schrödinger equation is that the wavefunction $\psi(y)$ could (for large y) be expanded in square-integrable functions of y (if $\alpha < \beta/2$). This is not a significant advantage for simple one-dimensional model problems which can be solved analytically, but it is important for problems which do not possess known analytic solutions for which basis set expansion techniques must be used.

3. Implications for Physically Realistic Problems

Having now illustrated how the exterior-scaled CRT is applied to "simple" piecewise potential problems, it is natural to ask whether difficulties arise in treating more physically realistic potentials (e.g., electron–atom or electron–molecule interactions). The answer is "usually not"! Because the electronic Schrödinger equation involves potentials which are globally defined (e.g., $-Z|r - R|^{-1}$) rather than given in a piecewise manner, one is not forced to address the question of matching ψ and ψ' at some boundary point. The usual (Coulombic) potentials and the square-integrable basis functions (e.g., Gaussian or Slater) which are commonly used are analytic functions of r. This "smoothness" property implies that, as r is "rotated" to $r \exp(i\alpha)$, ψ and ψ' will maintain their continuity (in r space). This point is very nicely made in ref. 5d, where Junker shows explicitly how the bound-state energies of the H atom are unchanged by rotation, and in ref. 5f where Doolen analyzes the exact expressions for the resonance energies and wavefunctions for a potential $(r^{-1} - \gamma r^{-2})$ which is supposed to describe e^+H atom scattering.

In a sense then, the simple one-dimensional square-well problems contain a confusing extra complication which does not arise in "usual" electronic structure considerations. However, it is a good idea to clarify the essential points. Lest the reader conclude that these remarks are essentially irrelevant because such difficulties arise only for piecewise potentials, it should be emphasized that exactly the same problems could arise in physically reasonable problems in which a wall or barrier is used to model a very repulsive region of (electronic) configuration space (e.g., for scattering of electrons from an atom sitting on a solid surface defined by $\theta = \Pi/2$, $0 \le \phi \le 2\Pi$, $0 \le r < \infty$ or for an electron–atom potential which is "cut off" at some small r value $r = r_0$). The rotation $\mathbf{r} = \mathbf{y} \exp(i\alpha)$ should only be used for $\mathbf{r}$ outside the surface "wall." Perhaps more importantly, for molecular problems in which the scaled nuclear attraction potentials are $-Z_A|r \exp(i\alpha) - R_A|^{-1}$ the cusp conditions obeyed by the wavefunction (and hence by the L^2 basis functions used to approximate ψ) at the nuclei will now (under rotation) be obeyed at the mathematical point $r = R_A \exp(-i\alpha)$. This cusp behavior is a straightforward consequence of the local $[\mathbf{r} \approx \mathbf{R} \exp(-i\alpha)]$ behavior of the Schrödinger differential equation. One could deal with this behavior in either of two ways. One could, as is suggested in ref. 11, not apply the rotation $\mathbf{r} = \mathbf{r}\exp(i\alpha)$ except for $|\mathbf{r}| > Z$ where Z is a distance greater than the maximum distance of any nucleus in the molecule from the one nucleus which is the coordinate origin. In this manner, one is guaranteed of scaling only the asymptotic part of the problem and the cusp behavior remains at $\mathbf{r} = \mathbf{R}$ (i.e., at real position). Alternatively, one could introduce into the basis (in addition to L^2 functions centered at $\mathbf{R}$) L^2 functions (in $\mathbf{r}$ space) centered at $\mathbf{R}\exp(-i\alpha)$. The Schrödinger equation can then "use" these new basis functions to force *proper* cusp behavior at $\mathbf{r}\exp(i\alpha) = \mathbf{R}$ [which is equivalent to $\mathbf{r} = \mathbf{R}\exp(-i\alpha)$] and the original L^2 basis functions centered at $\mathbf{R}$ to describe the large $\mathbf{r}$ behavior of ψ. Thus, in both cases the only thing which is accomplished by the coordinate rotation device is the modification of the asymptotic (large r) behavior of the resonance eigenfunctions in order to permit $\psi(r)$ [which obeys $H_\alpha(r)\psi(r) = E\psi(r)$] to be expanded in a square-integrable basis.

There are, of course, alternatives to using the CRT for finding resonance energies. Miller [13] has suggested that one essentially "skip" the coordinate rotation step and simply look directly for Siegert resonances. His method consists of carrying out a linear variational calculation using N square-integrable basis functions (determinantal configurations for a many-electron atom or molecule) and one "Siegert function" $\theta(r) = [1 - \exp(-r)]\exp(ikr)$ (or Siegert determinant containing all "bound" orbitals except for one orbital which is the result of orthogonalizing $\theta(r)$ to these bound orbitals). By extremizing $\langle\psi_t| -\frac{1}{2}(d^2/dr^2) + V(r) - \frac{1}{2}k^2|\psi_t\rangle$, where ψ_t is the trial linear variational wavefunction, one obtains a complex symmetric (k dependent) secular equation to solve. This secular equation is solved iteratively (guessing k, finding an eigenvalue and corresponding wavefunction ψ_j which is as close as possible to zero, using $2\langle\psi_j| - \frac{1}{2}(d^2/dr^2) + V|\psi_j\rangle$ as the next "guess" for k^2, etc.). The technical details of how this iterative process is carried out are discussed in ref. 13.

The primary difficulty which arises in using Miller's technique to search for Siegert resonances has to do with the evaluation of the Hamiltonian matrix element integrals involving the Siegert basis function $\theta(r)$. As the authors of refs. 13 clearly point out, these integrals can only be evaluated for $\mathrm{Im}\, k > 0$, whereas, as was stressed earlier in this article, the Siegert resonance energy has $\mathrm{Im}\, k < 0$. The response made by Miller et al. is to compute the integrals for $\mathrm{Im}\, k > 0$ and to continue these integrals simply analytically to $\mathrm{Im}\, k < 0$. This continuation is done either by replacing $\mathrm{Im}\, k$ by $-\mathrm{Im}\, k$, when the integrals are explicitly known functions of k, or by fitting the eigenvalue of the secular equation to a rational fraction in k and then replacing $\mathrm{Im}\, k$ by $-\mathrm{Im}\, k$ to obtain the "correct" eigenvalue (which gives their estimate of the Siegert resonance energy).

Although Yaris et al. [15] have shown how one can probably circumvent the divergent integrals which would arise in the application of Miller's approach with $\mathrm{Im}\, k < 0$, it is not entirely clear at this time whether this will turn out to be computationally more efficient than the coordinate rotation technique. It is the author's feeling that the direct search for Siegert resonances suggested by Miller et al. should be examined much more thoroughly, both from the formal and computational points of view. Certainly the initial applications of the method described in refs. 13 yielded very promising results.

4. Concluding Remarks

By considering the application of the so-called coordinate rotation technique together with exterior scaling ideas to two piecewise-defined one-dimensional "square-well" model potential problems, we have attempted to shed light on the mathematical structure of the rotated Schrödinger equation. In particular, we showed how to relate the nonasymptotic boundary condition appropriate to the rotated problem to those arising in the original (unrotated) Schrödinger equation. Hopefully, the result of these remarks is a clearer understanding of why the bound and resonance energy levels are not changed by rotation. The important effect of rotation is that the previously non-normalizable resonance wavefunctions become square integrable, hence making them amenable to approximations within commonly used basis sets.

In Sec. 3 we discussed under what circumstances the kind of boundary condition modification, which was essential for piecewise potentials, could arise in more physically relevant problems. Our primary conclusion was that such difficulties generally show up in electron–molecule or electron–atom scattering problems only at nuclear cusps or if one uses "hard wall" cutoff potentials to exclude the electron from certain regions of space as is commonly done when treating electron–atom scattering within the static exchange plus polarization model. One describes [15] the charge-induced dipole interaction of the electron with the target atom in terms of the target's polarizability a as $-a/2r^4$, $r_0 \leqslant r < \infty$, 0, $r < r_0$. Moreover, cusp conditions are not obeyed by the rotated electronic wavefunction for molecular problems (where one cannot take $R = 0$) at $r = R_A$, but rather, at $r = R_a \exp(-i\alpha)$ where r is the "rotated" coordinate. Analogous difficulties would result in attempting to use the coordinate rotation method in a straightforward manner while using Hartree–Fock orbitals computed using any type of hard-core pseudopotential method. The use of these piecewise potentials might be expected to present the kind of conceptual difficulties which we discussed in Sec. 2.

An alternative to searching for Siegert resonance states via the CRT was given by Miller et al. [13]. In Sec. 3 we presented some remarks concerning the relation of this method to the CRT and we pointed out the primary difficulty of the Miller approach. Although the numerical results obtained in refs. 13 are impressive and Yaris et al. [14] have demonstrated how one could avoid the divergent integrals arising in the original version of Miller's theory, it is not at all obvious that this direct Siegert search process will have any practical advantages over the CRT. It is the author's opinion that the ideal of Miller et al. is excellent and that we should proceed to develop a great deal more computational experience on model potential and realistic (*ab initio*) electron-atom and electron–molecule resonance problems.

Acknowledgments

The author thanks the University of North Carolina Chemistry Department for their hospitality during the fall of 1979, and the U.S. National Science Foundation for support in the form of Contract No. 7809734.

Appendix

The complex solutions to $\tan(kL) = -ik/\bar{J}$ can, of course, be found numerically for a given potential well depth (V) and length (L). However, to gain better insight into why these complex resonance solutions have a negative imaginary part it is instructive to attempt an approximate solution to the above equation. Toward this end, we consider the special case in which the potential well is deep and the kinetic energy of the incident electron is small (low-energy resonances). Then since $\bar{J} = (k^2 - 2V)^{1/2}$ is small, it is convenient to rewrite the resonance condition as $\tan[(\bar{J}^2 + 2V)^{1/2}L] = -i(\bar{J}^2 + 2V)^{1/2}/J$. Then, by factoring $(\bar{J}^2 + 2V)^{1/2} = (2V)^{1/2}(1 + \bar{J}^2/2V)^{1/2}$, expanding the square root in powers of $\bar{J}^2/V$, using $\tan(x + y) = (\tan x + \tan y)\,(1 - \tan x \tan y)$ and $\tan x \cong x$ for small x, one easily obtains

$$\tan(2VL^2)^{1/2} + [1 + \tan^2 (2VL^2)^{1/2}]\,\frac{\bar{J}^2 L}{2\sqrt{2V}} = -i\,\frac{\sqrt{2V}}{J}$$

If $\tan(2VL^2)^{1/2} \ll 1$, so that the well is nearly able to support a bound state having zero energy, we expect there to be a long-lived resonance state having slightly positive Re E. In this case, we obtain as a solution to the above resonance condition $\bar{J}^3 = -4iV/L$, which then implies $\bar{J} = (4V/L)^{1/3} \exp(-i\Pi/6)$, so that the resonance energy is $E = V + \frac{1}{2}(4V/L)^{2/3}\exp(-i\pi/3)$. Clearly this resonance root lies in the Im $E < 0$, Re $E < 0$ quadrant of the complex E plan as was claimed in Sec. 2. As the potential well depth is increased, E/V, which is the energy of the resonance in units of the well depth $[E/V = 1 + \frac{1}{2}(4/L)^{2/3}V^{-1/3}\exp(-i\Pi/3]$, comes closer and closer to unity. That is, the relative lifetime (in V energy units) of the resonance lengthens and the position (Re E) approaches the top of the potential well ($E = V$).

Bibliography

[1] D. J. Aguilar and J. Combes, Commun. Math. Phys. **22,** 269 (1971).

[2] E. Balslev and J. Combes, Commun. Math. Phys. **22,** 280 (1971).

[3] B. Simon, Commun. Math. Phys. **27,** 1 (1972).

[4] Int. J. Quantum Chem. **14**(4) (1978).

[5] (a) T. N. Rescigno, C. W. McCurdy, and A. E. Orel, Phys. Rev. A **17,** 1931 (1978); (b) G. D. Doolen, J. Nuttall, and C. J. Whery, Phys. Rev. Lett. **40,** 313 (1978); (c) J. J. Wendoloski and W. P. Reinhardt, Phys. Rev. A **17,** 195 (1978); (d) B. R. Junker, Int. J. Quantum Chem. **14,** 371 (1978), and references cited therein; (e) G. M. Doolen, J. Nuttal, and R. W. Stagat, Phys. Rev. A **10,** 1612 (1974); (f) G. Doolen, Int. J. Quantum Chem. **14,** 523 (1978).

[6] (a) C. W. McCurdy, Jr. and T. N. Rescigno, Phys. Rev. Lett. **41,** 1364 (1978); (b) M. Moiseyev and C. T. Corcoran, Phys. Rev. A (to be published).

[7] J. Nuttall and H. L. Cohen, Phys. Rev. **188,** 1542 (1969).

[8] (a) W. P. Reinhardt, Int. J. Quantum Chem. Quantum Symp. **10,** 359 (1976); (b) J. N. Bardsley and B. R. Junker, J. Phys. B **5,** L178 (1972); (c) A. P. Hickman, A. D. Isaacson, and W. H. Miller, Chem. Phys. Lett. **37,** 63 (1976); (d) G. D. Doolen, J. Phys. B **8,** 525 (1975); (e) H. S. Taylor and L. D. Thomas, Phys. Rev. Lett. **28,** 1091 (1972); (f) T. N. Rescigno and W. P. Reinhardt, Phys. Rev. A **8,** 2828 (1978); (g) R. T. Baumel, M. C. Crocker, and J. Nuttall, Phys. Rev. A **12,** 486 (1975); (h) T. N. Rescigno and W. P. Reinhardt, Phys. Rev. A **10,** 158 (1974); (i) T. N. Rescigno, C. W. McCurdy, Jr., and V. McKoy, J. Chem. Phys.

64, 477 (1976); (j) N. Moiseyev, P. R. Certain, and F. Weinhold, Mol. Phys. **36,** 1613 (1978); (k) P. Winkler and R. Yaris, J. Phys. B, 1481 (1978); (l) R. A. Bain, J. N. Bardsley, B. R. Junker, and C. V. Sukuman, J. Phys. B **7,** 2189 (1974).
[9] R. A. Donnelly and J. Simons, J. Chem. Phys. (to be published).
[10] C. Cerjan, R. Hedges, C. Holt, W. P. Reinhardt, K. Scheibner, and J. J. Wendoloski, Int. J. Quantum Chem. **14,** 393 (1978).
[11] B. Simon, Phys. Rev. Lett. **71A,** 211 (1979).
[12] A. J. F. Siegert, Phys. Rev. **56,** 750 (1939).
[13] (a) A. D. Isaacson, C. W. McCurdy, Jr., and W. H. Miller, Chem. Phys. **34,** 311 (1978); (b) A. D. Isaacson and W. H. Miller, Chem. Phys. Lett. **62,** 374 (1979).
[14] R. Yaris, R. Lovett, and P. Winkler, Chem. Phys. **43,** 29 (1979).
[15] H. A. Kurtz and Y. Öhrn, Phys. Rev. A **19,** 43 (1979).

Received March 14, 1980