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## The Siegert Method in Resonance Scattering: Relation to $L^2$ Methods

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In 1939 Siegert demonstrated [1] how one could obtain scattering resonance positions ( $\epsilon$ ), widths ( $\Gamma$ ), and lifetimes ( $\tau = \hbar/\Gamma$ ) by solving the Schrödinger equation under the constraint that the solution has no incoming wave amplitude. The imposition of this constraint gives rise to complex values for the resonance scattering energy ( $E = \epsilon - i\Gamma/2$ ). The resultant scattering wavefunction  $\psi$ , which in the asymptotic region contains only outgoing amplitude [exp(ikr)/r;  $k = \sqrt{2mE/\hbar^2}$ ], is not square integrable ( $L^2$ ) since exp(ikr) = exp( $i|k|r \cos\beta$ ) exp( $|k|r \sin\beta$ ) where  $k \equiv |k| \exp(-i\beta)$ . This non- $L^2$  nature of  $\psi$  has given rise to difficulties in applying Siegert's method (SM) to atomic [2] and molecular [3] autoionization processes.

Miller and co-workers recently have applied the SM to autoionizing states [2,3] by augmenting a standard  $(L^2)$  set of electronic basis functions with a "cut-off" Siegert function of the form  $[\exp(ikr)/r][1 - \exp(-r)]$ . The resulting secular equation was solved for its complex eigenvalues  $(E_j)$  which permitted k to be recalculated (as  $\sqrt{2mE_j/\hbar^2}$ ) to give a "new" Siegert function. This iterative procedure was carried to convergence at which one eignevalue  $E_j$  was equal to  $\hbar^2 k^2/2m$ . This eigenvalue then gave the resonance parameters  $\epsilon$  and  $\Gamma$  through  $E_j = \epsilon - i\Gamma/2$ .

As pointed out very clearly by Miller et al. in Refs. 2 and 3, the true Siegert functions [with Im(k) < 0] can not be used in a straightforward manner to compute matrix elements of the electronic Hamiltonian because of the divergent (for large r) behavior of exp(ikr)/r. The approaches taken in Refs. 2 and 3 to avoid this problem were to evaluate the requisite integrals over the Hamiltonian either with Im(k) replaced by -Im(k) [2] or with Im(k) slightly positive so that exp(ikr)/r is  $L^2$  [3]. That is, although the resonance energy and the true Siegert wavefunction have Im k < 0, the necessary integrals are evaluated for Im k > 0 and it is assumed that the resulting eigenvalues are independent of this fact (i.e., that  $E(k) = \hbar^2 k^2/2m$  is analytic in k). Yaris, Lovett, and Winkler [4] have pointed out that one could avoid the divergent integrals that arise from the true Siegert function. These authors thus demonstrated that the SM could be employed in a more straightforward manner [with Im(k) < 0, throughout]. The purpose of this letter is to shed further light upon this situation by showing that the "tricks" [replacing Im(k) by -Im(k) or by a small positive number] used by Miller et al. [2,3] are, in fact, valid because they can be viewed as nothing more than special coordinate rotation (CR) calculations involving  $L^2$  basis functions.

As Rescigno, McCurdy, and Ore [5] have suggested, it is possible, and probably even wise, to employ the coordinate rotation method (CRM) [6] to only the "active orbital" arising in electron-molecule collisions. The philosophy of the CRM [7,8] is that by "rotating" or scaling the coordinate of the scattering particles by an amount  $\exp(i\theta)$  ( $\mathbf{r} \rightarrow \exp(i\theta)\mathbf{r}$ ) either in the Hamiltonian (H) or in the "trial wavefunctions," one maps the non-L<sup>2</sup> resonance eigenfunctions of H into L<sup>2</sup> functions having the same resonance energies. The advantage of the CRM is that one can employ L<sup>2</sup> basis functions in electron scattering problems with  $\mathbf{r}_j$ replaced by  $\mathbf{r}_j \exp(i\theta)$ . In a many-electron problem, indistinguishability requires that the coordinates of all electrons be scaled by the same amount. The suggestion made in Ref. 6 is that one can scale a single orbital in any multi-electron Slater determinant; the antisymmetric nature of such determinants assures that indistinguishability is not violated. The physical motivation for considering this proposition is that only a single electron is unbound in the kind of electron-molecule scattering processes most commonly studied [2,3,4,6]; the remaining electrons are bound and should have their energy unchanged by coordinate rotation [5,6].

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It is now possible to show the connection between the "methods" used in Refs. 2 and 3 and the kind of CRM put forth in Ref. 6. If the Siegert function's asymptotic component  $\exp(ikr)/r$  is subjected to a rotation of magnitude  $\theta$ , it becomes proportional to  $\exp(i|k|r\cos(\theta - \beta))\exp(-|k|\sin(\theta - \beta))/r$  which is  $L^2$ . If the rotation angle  $\theta$  is chosen to be  $2\beta$ , then this rotated Siegert function is identical to that used in Ref. 2, where the Im $(k) \rightarrow -\text{Im}(k)$  device was used to make the Hamiltonian matrix elements calculable. The choice  $\theta = \beta + \delta$  ( $\delta$  is small and positive) leads to the modified Siegert wavefunction used in Ref. 3. As pointed out in Ref. 3, the latter approximation ( $\theta = \beta + \delta$ ) seems to work better than the Im $(k) \rightarrow -\text{Im}(k)$ . This is not at all surprising to one who is familiar with applications of the CRM. It is well known that the desired resonance eigenvalues remain relatively stable (to  $\theta$  variation) near  $\theta = \beta$ , whereas the (unavoidable) use of finite basis sets makes these eigenvalues quite  $\theta$ -dependent for  $\theta \gg \beta$  (e.g.,  $\theta = 2\beta$ ). In future applications of the Siegert method, it is suggested either that one exploit the developments made by Yaris et al. [4] to completely avoid divergent integrals [for Im(k) < 0] or that one use the  $\theta = \beta + \delta$  device to "rotate" the Siegert function into the  $L^2$  class upon which the desired resonance eigenvalue  $E_j = \hbar^2 k^2/2m$  should be (relatively)  $\theta$ -independent.

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