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Should one use complex basis functions in coordinate rotation calculations on molecules?

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In applying the coordinate rotation method¹ (CRM) to electron-molecule² scattering resonances, one attempts to find the complex eigenvalues (Z_α) corresponding to square integrable eigenfunctions (ψ_α) of the rotated Hamiltonian H_η . H_η is obtained from the conventional Hamiltonian by scaling the electronic coordinates \mathbf{r}_i by the complex quantity $\eta(\mathbf{r}_i - \mathbf{r}_i\eta)$. For a diatomic molecule whose nuclei have charges Z_A , Z_B and positions \mathbf{R}_A , \mathbf{R}_B , H_η contains kinetic energy ($-\eta^2/2\sum_i^N \nabla_{\mathbf{r}_i}^2$), electron-electron interactions ($\eta\sum_{i<j}^N r_{ij}^{-1}$), and electron-nuclei interactions ($-\eta\sum_i^N Z_A|\mathbf{r}_i - \eta^{-1}\mathbf{R}_A|^{-1} - \eta\sum_i^N Z_B|\mathbf{r}_i - \eta^{-1}\mathbf{R}_B|^{-1}$). The desired resonance eigenvalues of H_η are usually found by expanding $\psi_\alpha(\mathbf{r})$ in some basis of square integral functions ($\psi_\alpha \cong \sum_k C_k(\eta)\phi_k(\mathbf{r})$) which are themselves real and η -independent. If the basis set $\{\phi_k(\mathbf{r})\}$ is complete, this is a perfectly reasonable expansion to make. However, in practical applications of the CRM to electron-molecule scattering, the set $\{\phi_k\}$ usually consists of a finite number of $(N+1)$ electron Slater determinants involving molecular orbitals expressed in terms of atomic orbitals centered at \mathbf{R}_A and \mathbf{R}_B . This set is certainly not complete, so it is quite natural to ask whether it is even reasonable to employ this particular choice of basis.

It is well known³ that the lowest energy eigenfunctions of the unscaled Hamiltonian [$H(\eta=1)$] possess high amplitude near each of the two nuclei. This arises because the Schrödinger equation is dominated, for $\mathbf{r}_i = \mathbf{R}_A$, by $-\frac{1}{2}\nabla^2 \mathbf{r}_i^2 - Z_A|\mathbf{r}_i - \mathbf{R}_A|^{-1}$ which, just as in the hydrogen atom, gives large (1s) amplitude in \mathbf{r}_i space near \mathbf{R}_A . In choosing atomic orbital basis sets for use in standard variational calculations on $H(\eta=1)$, it is important to include functions which properly represent the locally high amplitudes near \mathbf{R}_A , because of the strong influence of this part of the electron density on the total electronic energy. It is most common to employ either 1s Slater or "tight" contracted Gaussian basis functions centered at \mathbf{R}_A and \mathbf{R}_B .

In considering the best choice of basis for treating the rotated H_η , it therefore seems important to guarantee that the resultant approximations to $\psi_\alpha(\mathbf{r})$ display high

orbital amplitude at points dictated by H_η . Because the electron-nuclei interactions in H_η have singularities at $\mathbf{r}_i = \eta^{-1}\mathbf{R}_{A,B}$, it is probably quite important to include in any reasonable atomic orbital basis (Slater or Gaussian) functions centered at the complex positions $\eta^{-1}\mathbf{R}_A$ and $\eta^{-1}\mathbf{R}_B$. This is easily achieved in electron-atom problems by simply choosing the coordinate origin to be at the atomic nucleus; then $\eta^{-1}\mathbf{R}_A = \mathbf{R}_A = \mathbf{0}$. For molecules, this choice of origin does not remove the problem.

Because the most common procedures^{1,2} for locating resonance energies (Z_α) within the CRM involve following eigenenergies of H_η as η is varied, all η -dependent atomic-basis integrals (one- and two-electron) arising in the computation (e.g., by configuration interaction) of Z_α need to be recomputed. We therefore suggest that one employ only a few (e.g., one per nucleus) "tight" basis functions centered at $\eta^{-1}\mathbf{R}_A$, $\eta^{-1}\mathbf{R}_B$, while using large numbers of atomic orbitals centered at \mathbf{R}_A , \mathbf{R}_B . The latter basis functions should be capable of describing the resonance wave function $\psi_\alpha(\mathbf{r})$ in the "valence" region and for values of \mathbf{r} which are on the "exterior" of the target molecule. Moreover, only those integrals which involve the functions centered at $\eta^{-1}\mathbf{R}_A$ or \mathbf{B} need to be recomputed as η is varied.

If the basis $\{\phi_k\}$ is not able to describe high orbital amplitudes at $\eta^{-1}\mathbf{R}_{A,B}$ then spurious imaginary contributions⁴ can arise in the desired resonance energies and even in the bound states which should be η -independent. We believe that the "compromise basis" described above has potential for eliminating the undesirable spurious features. Rescigno *et al.*⁴ and Junker *et al.*⁴ have, in fact, already employed an approach which is similar to that being proposed here. For example, Rescigno *et al.* employ a Slater determinant basis in which the N "bound" orbitals of the target atom are not even rotated (in our language, this would be analogous to expanding the N bound orbitals in terms of the basis orbitals centered at $\eta^{-1}\mathbf{R}_{A,B}$, which essentially "undoes" the effort of rotating these N electrons in H_η). Only the "active" $N+1$ st orbital is rotated. There is only a slight difference between what we are proposing and what

was used in Refs. 4. We prefer to permit the rotated Schrödinger equation $(H_\eta - Z)\psi = 0$ to "decide" how much of the basis orbitals at $\eta^{-1}\mathbf{R}_{A,B}$ to use; in Refs. 4, the target atom is required to use only these orbitals.

Because of the proven numerical success of the approach advocated here as documented in a somewhat limited form in Refs. 4, we believe that it is quite wise for researchers in this area to implement such "mixed" basis sets.

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Orbiting trajectories in noncentral fields^{a)}

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An attractive central potential that falls off faster than $1/r^2$ admits orbiting trajectories at all sufficiently low positive energies. These are circular trajectories, $r(t) = r_{orb}(E)$, on which the centrifugal force just balances the attraction to the center. There is a natural distinction between "soft" and "hard" collisions at an orbiting energy E : no trajectory with impact parameter greater than the orbiting impact parameter $b_{orb}(E)$ reaches the surface $r = r_{orb}(E)$, while all trajectories with impact parameter less than $b_{orb}(E)$ not only penetrate this surface but also reach some second, inner surface $r < r_{orb}(E)$. The "boundary" trajectories separating hard from soft collisions—the trajectories with $b = b_{orb}(E)$ —are asymptotic, as $t \rightarrow \infty$, to the orbiting trajectories.

Orbiting in a central field therefore suggests a natural definition of "collision complex," a definition that is used in the familiar Langevin theory of ion-molecule collisions¹ and in Light's phase-space theory of chemical reactions.²

In this note we show that orbiting trajectories exist in noncentral fields as well and serve the same purpose of separating soft from hard collisions.

Consider first the motion of a particle of energy E in the field of a fixed potential $V(r)$. We suppose that there exists a smooth closed surface in r space—for example, the surface of a sphere—with the following property: Any trajectory of energy E that is tangent at $t=0$ to any point on the surface spends all sufficiently small $t \neq 0$ inside the surface. We suppose, in other words, that the energy is low enough and the potential sufficiently attractive that all trajectories tangent to the surface curve toward the inside more strongly than does the surface itself. If the surface is that of a sphere, for example,

we demand that at every point the radial force in exceed the centrifugal force out:

$$\partial V / \partial r > 2\{E - V(r)\} / r. \quad (1)$$

It is easy to see that in the case of a central potential Eq. (1) is a sufficient condition for orbiting.

Given such a surface, we shall use the following obvious consequence: Any trajectory of energy E that meets the surface, coming from the outside, in fact crosses the surface and enters the interior.

We shall need a second surface, the surface of a large sphere entirely surrounding the first surface, with this property: Any trajectory of energy E that is tangent at $t=0$ to any point on the surface spends all sufficiently small $t \neq 0$ outside the surface. Such a surface always exists: we just choose it so far from the region of the potential that trajectories tangent to it are essentially free-particle trajectories. Trajectories that meet this outer surface, coming from the inside, must cross the surface and enter the exterior.

Between the inner and outer surfaces lies an open region R of r space. We shall show that there are orbiting trajectories of energy E in this region.

Consider a beam of particles of energy E incident on the potential. We label each trajectory $r(t, b)$ by the point b at which it crosses a plane perpendicular to the beam in the asymptotic entrance region, and we specify that each trajectory cross this plane at $t=0$, $r(0, b) = b$. A subset of these trajectories will cross the outer surface and enter region R ; the corresponding set of points in the b plane is open and connected. Subsequently, each of these trajectories suffers one of three fates: the trajectory first leaves region R through the outer sur-