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Complex-rotated Hartree-Fock method and its application to the Be$^-$ shape resonance

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A complex-coordinate rotation has been applied to the standard Hartree-Fock equations, in order to form a complex-rotated Hartree-Fock procedure. The resulting complex differential equations were solved by direct numerical integration. This method was then used to study the position and width of the ^2P shape resonance in Be$^-$. The results were found to be quite independent of the value of the rotation angle θ for θ greater than the value at which the complex pole was uncovered.

I. INTRODUCTION

A recent addition to the calculation methods available to atomic and molecular theorists is the complex-coordinate-rotation method.[1-3] This method, which is based on the rotation of the electron coordinates into the complex plane, is now being used in a wide variety of ways to calculate atomic and molecular resonances. Resonance states are typically described as having a complex energy

$$E=E_R+iE_I=E_R-i(\Gamma/2)\ , \tag{1}$$

where E_R corresponds to the position of the resonance and E_I corresponds to the width, or inverse lifetime, of the resonance. The purpose of the complex rotation method is to produce a non-Hermitian Hamiltonian whose eigenvalues are given by Eq. (1).

The fundamental transformation of the complex rotation methods is, in the atomic case,

$$r\rightarrow re^{i\theta}\ , \tag{2}$$

where r is the electron radius. This rotation has two effects on the calculation of the energy and wave function of a resonance. The pole corresponding to the resonance energy is generally thought to be located on a higher sheet of the Riemann surface where it is "hidden" by the first sheet. The rotation by Eq. (2) has the effect of shifting the energy axis in order to "expose" the resonance pole, allowing it to be calculated.[3] Furthermore, the wave function associated with the resonance is transformed from an unbound, non-L^2-normalizable form to a boundlike, albeit complex, wave function.

The complex-coordinate-rotation methods has traditionally been applied to basis-set calculations of one type or another. Two of the more widely used applications are to the configuration-interaction approach[4] or to a basis-set solution of the Hartree-Fock equation.[5] To our knowledge, no application has been made to the standard self-consistent form of the Hartree-Fock method,[6] where the atomic wave function is found by direct numerical integration of the Hartree-Fock equation.

In this work we apply the complex-coordinate-rotation transformation to the numerical Hartree-Fock method in order to produce a general *ab initio* calculation method capable of directly solving for atomic resonances. As a test case, we apply this complex-rotated Hartree-Fock method to the lowest ^2P shape resonance in Be$^-$.

II. THEORY

We begin by performing the rotation of r into the complex plane upon the nonrelativistic atomic Hamiltonian

$$\mathscr{H}=\sum_{i=1}^{N}\left(-\tfrac{1}{2}\nabla_i^2-Z/r_i\right)+\sum_{\substack{i,j\\(i<j)}}1/r_{ij}\ , \tag{3}$$

producing

$$\mathscr{H}(\theta)=\sum_{i=1}^{N}\left(-\tfrac{1}{2}\nabla_i^2e^{-2i\theta}-e^{-i\theta}Z/r_i\right)+\sum_{\substack{i,j\\(i<j)}}e^{-i\theta}/r_{ij}\ . \tag{4}$$

Notice that while the kinetic energy term is rotated by $e^{-2i\theta}$, the potential energy terms are rotated by $e^{-i\theta}$. We now wish to use the Hartree-Fock method to solve the complex energy eigenvalue equation formed by this operator

$$\mathscr{H}(\theta)\psi(\theta)=(E_R+iE_I)\psi(\theta)\ . \tag{5}$$

The complex eigenvalue of this equation define the energies and widths of atomic resonances and the complex eigenfunctions are L^2. The Hartree-Fock equation is derived in the ordinary sense by setting to zero the variations of the energy with respect to the atomic orbitals. The energy functional to be varied is given by the expectation value of the Hamiltonian with respect to the atomic wave function ψ, plus Langrange multiplier terms which preserve orthonormality. A difficulty arises in the rotated system due to the non-Hermitian nature of $\mathscr{H}(\theta)$. That is, the eigenfunctions of $\mathscr{H}(\theta)$ form a biorthogonal set[1] instead of the normal simpler orthonormal set. This leads to left and right eigenvectors and a complication in the description of the expectation value of the energy. We follow the standard procedure in this case[5,7] and define our energy functional as

$$W=\langle\psi(\theta)\,|\,\mathscr{H}(\theta)\,|\,\psi(\theta)\rangle+\sum_{a}\lambda_a(\theta)\langle\phi_a(\theta)\,|\,\phi_a(\theta)\rangle + \sum_{\substack{a,b\\(a\neq b)\\(l_a=l_b)}}\lambda_{ab}(\theta)\langle\phi_a(\theta)\,|\,\phi_b(\theta)\rangle\ . \tag{6}$$

Here the complex part of ψ that is due to the rotation of r is not complex conjugated when the bra state is formed but the normally complex parts of the wave function, such as in the angular factors, are treated in the standard fashion. The λ's in Eq. (6) are the complex equivalents of the Lagrange multipliers designed to preserve orthonormality. We have assumed here that the total wave function ψ is composed of a Slater determinant of spin orbitals ϕ_a which can be separated into radial and angular components,

$$\phi_a=\frac{1}{r}P_{nl}(r)Y^{l}_{m_l}(\theta,\psi)\chi_{m_s}\ . \tag{7}$$

Upon variation of the energy functional W with respect to ϕ_a, the complex differential equation for the radial wave function P_a becomes

$$\begin{aligned}L(\theta)(P_{Ra}+iP_{Ia})&=\frac{2e^{-i\theta}}{r}(Y_{Ra}+iY_{Ia})(P_{Ra}+iP_{Ia})\\&\quad+(X_{Ra}+iX_{Ia})+(\epsilon_{Ra}+i\epsilon_{Ia})(P_{Ra}+iP_{Ia})\\&\quad+\sum_{\substack{b\\(b\neq a)\\(l_b=l_a)}}(\epsilon_{Rab}+i\epsilon_{Iab})(P_{Rb}+iP_{Ib})\ ,\end{aligned} \tag{8}$$

where we have used

$$L(\theta)=e^{-2i\theta}\frac{d^2}{dr^2}+e^{-i\theta}\frac{2Z}{r}-e^{-2i\theta}\frac{l(l+1)}{r^2}\ . \tag{9}$$

Y_a and X_a in Eq. (8) stand for the direct and exchange potentials associated with the orbital a. P_{Ra} and P_{Ia} are the real and imaginary parts of the radial wave function and ϵ_R and ϵ_I are the real and imaginary parts of the energy parameters that come from the Lagrange multipliers.[6] The potential terms that constitute Y_a and X_a are found by directly rotating, with $r\to re^{i\theta}$, their standard real form. For example, the direct potential Y_a is composed of terms of the form $Y^K(a,b)$ where[6]

$$Y^K(a,b)=r\int_0^\infty \frac{r_<^K}{r_>^{K+1}}P_a(r_1)P_b(r_1)dr_1\ . \tag{10}$$

This becomes, upon rotation,

$$\begin{aligned}Y^K_R(a,b)+iY^K_I(a,b)&=re^{i\theta}\int\frac{1}{e^{i\theta}}\left[\frac{r_<^K}{-r_>^{K+1}}\right](P_{Ra}+iP_{Ia})\\&\qquad\times(P_{Rb}+iP_{Ib})dr_1e^{i\theta}\ .\end{aligned} \tag{11}$$

Similar rotations are performed on the $Y^k(a,b)P_b$ terms which comprise X_a. The inclusion of the Lagrange multipliers forces orthonormality on our complex orbitals under the form

$$\delta_{ab}=\int_0^\infty (P_{Ra}+iP_{Ia})(P_{Rb}+iP_{Ib})e^{i\theta}dr\ . \tag{12}$$

The boundary conditions imposed on the wave functions which are solutions of Eq. (8) are similar to those imposed by standard Hartree-Fock (HF) theory. For bound-state orbitals, whose general form is

$$\sum_n a_nr^ne^{-Kr}\ , \tag{13}$$

the rotation to

$$\sum_n a_n(\theta)r^ne^{in\theta}e^{-Kr\cos\theta}e^{-iKr\sin\theta} \tag{14}$$

produces no difficulties because the $\exp[-Kr\cos(\theta)]$ factor forces the same asymptotic behavior as does $\exp(-Kr)$. That of course implies that $\theta<\pi/2$, a restriction we must observe rigorously. On the other hand, the general asymptotic form of a resonance state can be written[2]

$$e^{iKr}/r\ , \tag{15}$$

where K is a complex number $[\,|K|\exp(-i\beta)]$. Such a state has an energy which is given by Eq. (1). The wave function of Eq. (15) is exponentially divergent at large r ($\beta>0$), but rotation by an angle θ produces the asymptotic form

$$\frac{e^{ikre^{i(\theta-\beta)}}}{re^{i\theta}} \tag{16}$$

which is L^2 for $\theta>\beta$. Therefore, we require that, for $\theta>\beta$, the real and imaginary parts of these now bound orbitals approach zero as $r\to0$ and $r\to\infty$.

If we multiply Eq. (8) through by $\exp(2i\theta)$ we can rewrite it as (dropping the subscript a)

$$\frac{d^2}{dr^2}(P_R+iP_I)=(F_R+iF_I)(P_R+iP_I)+(G_R+iG_I)\ , \tag{17}$$

thus producing a complex, inhomogeneous differential equation for P. The differential equation which is solved by a standard Hartree-Fock program (we follow here the multiconfiguration Hartree-Fock program of Fischer[8]) has the form

$$\frac{d^2}{dr^2}P=FP+G\ . \tag{18}$$

The general solution of Eq. (18) is $P=P_{\text{in}}+\alpha P_{\text{ho}}$, where P_{in} is any solution to the inhomogeneous equation and P_{ho} is a solution of Eq. (16) when $G\equiv0$. Unfortunately, there are no numerical integration techniques which function properly over the entire range of r. Consequently, numerical integration of Eq. (18) must be broken into two parts, one over the region closer to the origin, and the other encompassing the region of large r. These numerical integrations are performed on a set of grid points which define r. The grid point J where the two integration routines meet is determined by the form of the direct potential.[6] The outward integration, from $r=0$ to $r=J$, is performed with a numerical technique called the shooting method,[6] and the integration in the large-r region is performed using a different numerical technique, the refined direct method.[6] This latter method uses as an initial point the value of J, and satisfies the boundary condition at infinity by forcing $P=0$ at some point M. These two solutions are forced to match at the point $J+1$ (recall that they are already equal at J), which allows us to solve for α. This procedure produces the new HF orbital P',

We use basically these same techniques to integrate the complex form of the Hartree-Fock equation (17). Since we wish to perform only real numerical integrations, Eq. (17) must first be split up into separate equations for P_R and P_I,

$$\frac{d^2}{dr^2}P_R=F_RP_R-F_IP_I+G_R \tag{19a}$$

and

$$\frac{d^2}{dr^2}P_I=F_RP_I+F_IP_R+G_I \; . \tag{19b}$$

Since Eqs. (19) are obviously coupled, the two real integrations must be performed simultaneously. If we rewrite Eqs. (19) in matrix form

$$\frac{d^2}{dr^2}\begin{bmatrix} P_R \\ P_I \end{bmatrix}=\begin{bmatrix} F_R & -F_I \\ F_I & F_R \end{bmatrix}\begin{bmatrix} P_R \\ P_I \end{bmatrix}+\begin{bmatrix} G_R \\ G_I \end{bmatrix} , \tag{20}$$

we see that, by setting $G\equiv 0$, the homogeneous form of the differential equations is

$$\frac{d^2}{dr^2}P_R=F_RP_R-F_IP_I \tag{21a}$$

and

$$\frac{d^2}{dr^2}P_I=F_RP_I+F_IP_R \; . \tag{21b}$$

One therefore performs the two real integrations of Eqs. (21) for the homogeneous solution and of Eqs. (19) for the inhomogeneous solution, and the complex coefficient α is found by matching the complex wave functions at the point $J+1$. The new orbital P' is then normalized by finding the coefficients C_R and C_I under the condition

$$1=\int_0^\infty (C_R+iC_I)^2(P'_R+iP'_I)^2e^{i\theta}dr \; . \tag{22}$$

III. CALCULATION

As a test of this complex-coordinate-rotated Hartree-Fock method, we studied the lowest ^2P shape resonance in electron-beryllium scattering. We performed a completely self-consistent, rotated HF calculation on this system by allowing each orbital to vary for some given θ. The calculation was then repeated at different θ's to ascertain the θ dependence of the solutions. The calculation was first performed on the isoelectronic relative of Be$^-$, neutral boron. Boron is of course a stable atom with naturally bound orbitals, and corresponding real eigenvalues. This calculation converged quite rapidly and produced a total energy of $E_R=-24.529\,11$ a.u. and $E_I=-5.510\times10^{-5}$ a.u. for $\theta=0.35$. The result obtained by an unrotated HF calculation, to which our method should be equal, was $E=-24.529\,06$ a.u. We therefore have an overall error in the calculation of order 10^{-5} a.u. The energy of the rotated system was found to be independent of θ to roughly the same order, i.e., to about 10^{-5} a.u.

We move now to the resonance problem of the beryllium negative ion. Again, a fully self-consistent calculation was performed where all the orbitals were allowed to vary, subject to the orthonormality restrictions. As starting values for the orbitals, rotated Roothaan-Hartree-Fock[9] orbitals were used for the core $1s$ and $2s$ wave functions and a rotated screened hydrogenic orbital (with $Z_{\text{eff}}=1.0$) was used for the resonance p wave function. As in the neutral case, the complex energy turned out to be independent of θ to order 10^{-5} a.u. This is a somewhat surprising result that we discuss further below. The results obtained for the complex energy range from $E_R=-14.547\,77$ a.u. and $E_I=-9.394\times10^{-3}$ a.u. for $\theta=0.28$ to $E_R=-14.547\,78$ a.u. and $E_I=-9.446\times10^{-3}$ a.u. for $\theta=0.49$. The energy obtained from a HF calculation for the neutral beryllium atom was $-14.573\,06$ a.u. giving a value of 0.025 a.u. for the ener-

TABLE I. Calculations on the lowest ^2P shape resonance of Be$^-$.

Calculation	Method	E_R (a.u.)	Γ (a.u.)
Present work	Complex-rotated Hartree-Fock	0.025	0.018
McNutt and McCurdy[a]	Complex-rotated self-consistent field Slater basis	0.025	0.019
Rescigno *et al.*[b]	Static exchange, complex coordinates	0.028	0.060
Hunt and Moiseiwitsch[c]	Local potential model	0.022	0.008
Donnely and Simons[d]	Second-order electron propagator	0.021	0.036

[a] Reference 10.
[b] Reference 11.
[c] Reference 12.
[d] Reference 13.

gy of the resonance state above the ground state of beryllium. There is no experimental data for this resonance at present, but many theoretical calculations exist.[10–13] Results obtained in these other calculations were compared to our results in Table I. Our values seem to be in quite good agreement with those of McNutt and McCurdy.[10]

The lack of significant θ dependence of our results is quite interesting. In most other complex rotation calculations, the θ dependence of the energy is quite pronounced. In cases in which a strong θ dependence is observed, the energy of the resonance is determined from a θ diagram by finding a point, where $E(\theta)$ seems to stable. These diagrams, which are constructed by plotting the complex energy as a function of θ, can be quite bizarre in appearance.[4,14] It has been suggested to us[15] that the θ-independent result is due to the fact that we have numerically integrated the HF equations. It was hypothesized some time ago that an exact resonance wave function can be represented by a power series in $re^{i\theta}$ whose coefficients are independent of θ for $\theta > \beta$.[1] The supposition is then that our numerical technique correctly embodies this θ dependence into our rotated wave function. Preliminary examination of this conjecture proved inconclusive. If this conjecture is true, it would be powerful argument for using this form of the complex-coordinate rotation rather than a basis-set approach. We are hopeful that future work in this area will clear up this point.

IV. CONCLUSION

We have developed a calculation method which is the complex-rotation form of the Hartree-Fock method. We have solved the Hartree-Fock equation in the rotated space in the standard way, that is by direct integration of the differential equation. At this point, the calculation has only been developed for single-configuration wave functions, which restricts our analysis to shape resonances only. The obvious next step is a multiconfiguration form which will allow configuration-interaction effects, such as Feshbach resonances, to be examined. The success of the calculation in the Be^- case is encouraging enough to proceed to the more general case.

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[1] B. R. Junker, in *Advances in Atomic and Molecular Physics,* edited by D. Bates and B. Bederson (Academic, New York, 1982), Vol. 18.

[2] W. P. Reinhardt, Annu. Rev. Phys. Chem. **33**, 223 (1982).

[3] Y. K. Ho, Phys. Rep. **99**, 1 (1983).

[4] G. D. Doolen, J. Phys. B **8**, 525 (1975).

[5] C. W. McCurdy, T. N. Rescigno, E. R. Davidson, and J. G. Lauderdale, J. Chem. Phys. **73**, 3268 (1980).

[6] C. F. Fischer, *The Hartree-Fock Method for Atoms* (Wiley, New York, 1977).

[7] K. T. Chung and B. F. Davis, Phys. Rev. A **26**, 3278 (1982).

[8] C. F. Fischer, Comput. Phys. Commun. **14**, 145 (1978).

[9] E. Clementi, *Tables of Atomic Functions* (IBM, New York, 1965).

[10] J. F. McNutt and C. W. McCurdy, Phys. Rev. A **27**, 132 (1983).

[11] T. N. Rescigno, C. W. McCurdy, and A. E. Orel, Phys. Rev. A **17**, 1931 (1978).

[12] R. A. Donnelly and J. Simons, J. Chem. Phys. **73**, 2858 (1980).

[13] J. Hunt and B. L. Moiseiwitsch, J. Phys. B **3**, 892 (1970).

[14] O. Atabek, R. Lefebure, and A. Reguena, Chem. Phys. Lett. **78**, 13 (1981).

[15] B. R. Junker (private communication).