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Coordinate Rotated TDHF Excitation Energies Li$^-$ $^1S \rightarrow {}^1P$

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Abstract

We present the first application of the coordinate rotation method, within the time-dependent Hartree–Fock framework, to calculation of positions and widths of metastable excited states. The method is briefly outlined and results of its application to ^1P excited states of Li$^-$ are given. Comparison of our results to those obtained using electron scattering methods by other workers is also made.

1. Introduction

Here we report the first application of the complex coordinate rotation (CCR) technique [1] to the time-dependent Hartree–Fock (TDHF) polarization propagator [2]. This propagator gives approximate electronic excitation energies of the systems for which it is calculated. The coordinate rotation technique permits us to select those excitation energies which show resonance behavior and hence correspond to metastable excited states of the system. In an ideal case, the energies of bound excited states should not be affected by the rotation, whereas the energies of unbound scattering and resonance states should show the kind of behavior described in Ref. 1. Since the result of a propagator calculation gives *differences* between a bound state (the so-called reference state which is usually the ground state) and excited states (some of which are unbound), we should see analogous behavior manifested in the excitation energies corresponding to unbound excited states. Before presenting and discussing the results of the first such applications of the complex coordinate rotation method, we review the tools of propagator theory and we show how these tools are extended to the complex rotation case.

2. Review of Propagator Theory

Normally the general propagator is defined [2] as follows:

$$\langle\langle A(t); B(t')\rangle\rangle = -i\theta(t-t')\langle A(t)B(t')\rangle \pm i\theta(t'-t)\langle B(t')A(t)\rangle, \tag{1}$$

where θ is the Heaviside function [$\theta(t)=1$ if $t>0$; $\theta(t)=0$ if $t<0$] and A and B are arbitrary Heisenberg-type operators in second quantization form. If A and B are bosons (i.e., if they conserve electron number), one should use the minus sign on the second term above; in the case of fermions, the plus sign is

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used. For the polarization propagator, operators A and B are both the electric dipole operator, which is expanded in the (boson) form

$$\mathbf{r}_{\mathrm{op}}=\sum_{rs}(\mathbf{r})_{sr}s^{\dagger}r, \tag{2}$$

where

$$(\mathbf{r})_{sr}=\int U_s^{*}\,\mathbf{r}\,U_r\,d\sigma. \tag{3}$$

Here $\{U_s\}$ is a set of orthonormal spin orbitals, whose exact nature is discussed below, and $s^{\dagger}$ and r are the electron creation and annihilation operators corresponding to orbitals U_s and U_r. The integral over $d\sigma$ refers to integration over space and spin coordinates. By taking $t'=0$, the above propagator can be rewritten, for A and B equal to the dipole operator, as

$$\langle\langle A(t);B\rangle\rangle=-i\theta(t)\langle A(t)B\rangle-i\theta(-t)\langle BA(t)\rangle. \tag{4}$$

Then using the fact that the Heisenberg operator $A(t)$ has the form

$$A(t)=\exp(iHt)A\exp(-iHt), \tag{5}$$

and inserting a resolution of the identity between A and B, we can write the following formally exact expression:

$$\begin{aligned}\langle\langle A(t);B\rangle\rangle=\sum_n\{&-i\theta(t)\exp[it(E_0-E_n)]\langle 0|A|n\rangle\langle n|B|0\rangle\\&-i\theta(-t)\exp[-it(E_0-E_n)]\langle 0|B|n\rangle\langle n|A|0\rangle\},\end{aligned} \tag{6}$$

where $|0\rangle$ is the exact ground state and the set of functions $\{|n\rangle\}$ is assumed to consist of the exact eigenstates of H. The Fourier transform $\langle\langle A;B\rangle\rangle_E$ of the above propagator is defined as

$$\langle\langle A;B\rangle\rangle_E\int_{-\infty}^{\infty}dt\,\langle\langle A(t);B\rangle\rangle\exp(iEt)\exp(-\eta|t|), \tag{7}$$

which leads to

$$\langle\langle A;B\rangle\rangle_E=\lim_{\eta\to 0+}\sum_n\left(\frac{\langle 0|A|n\rangle\langle n|B|0\rangle}{E-E_n+E_0+i\eta}-\frac{\langle 0|B|n\rangle\langle n|A|0\rangle}{E-E_0+E_n-i\eta}\right) \tag{8}$$

where η originates from the convergency factor $\exp(-\eta|t|)$ used in defining the Fourier transform. The energy differences E_n-E_0 appearing in the denominators of $\langle\langle A;B\rangle\rangle_E$ give rise to poles corresponding to excitation energies.

The introduction of the rotated Hamiltonian [1, 3] $H[\mathbf{r}\alpha\exp(i\theta)]=H(\xi)$ (α and θ are real parameters) gives rise to a modified polarization propagator. Instead of using eigenstates of H in Eq. (6) one now has to use [3] eigenstates of the rotated $H(\xi)$, as a result of which the eigenvalues E_0, E_n become eigenvalues of $H(\xi)$. For bound states, these eigenvalues will be the same as before (although the eigenstates are different), while for unbound states they will be changed. The poles of the resulting propagator will then occur at the rotated Henergy differences which will, in general, be complex.

The actual evaluation of the propagator is performed by using the super-operator formalism described in Ref. 4, from which one obtains an equation of the form

$$\langle\langle A; B\rangle\rangle_E = (A|\mathbf{h})(\mathbf{h}|E\hat{I} - \hat{H}|h)^{-1}(\mathbf{h}|B), \tag{9}$$

where the super operators $\hat{H}$ and $\hat{I}$ are defined by

$$\hat{H}X_J = [H, X_J]_-;\ \hat{I}X_J = X_J \tag{10}$$

and the "binary product" by

$$(X_J|X_i) = \langle 0|[X_J^\dagger, X_i]_-|0\rangle. \tag{11}$$

In this formalism, the singularities of the matrix $(\mathbf{h}|E\hat{I} - \hat{H}|\mathbf{h})^{-1}$ correspond to the poles of the propagator given in Eq. (8).

The introduction of the rotated $H(\xi)$ into the definition of the polarization propagator requires [3] that the reference state $|0\rangle$ used in the definition of the super operator "binarry product" be an eigenstate of $H(\xi)$, *not* of H. This follows because we assumed that $H(\xi)|0\rangle = E_0|0\rangle$, and, although E_0 is unchanged relative to its unrotated value, $|0\rangle$ is no longer the "unrotated" eigenfunction of H. Hence, in Eqs. (9)–(11), $|0\rangle$ refers to the "rotated" reference state and H refers to $H(\xi)$.

In the single-configuration formulation of the above outlined theory, one introduces the following approximations:

(i) $|0\rangle$ is assumed to be a single determinant Hartree–Fock state $|\text{HF}\rangle$ consisting of orbitals which have been coordinate rotated to make $|\text{HF}\rangle$ an approximate eigenstate of $H(\xi)$.

(ii) The operator space $\mathbf{h}$ is limited to single particle–hole and hole–particle operators $\mathbf{h}_2$ defined as $\mathbf{h}_2 = \{m^\dagger\alpha; \alpha^\dagger m\} = \{q^\dagger_{m\alpha}; q_{m\alpha}\}$, where the Greek letters refer to spin orbitals occupied in $|\text{HF}\rangle$ and the Roman letters to spin orbitals unoccupied in $|\text{HF}\rangle$. These operators are collected into column vectors $\mathbf{q}^\dagger$ and $\mathbf{q}$ below in writing expressions for the matrix elements needed to compute the polarization propagator. This choice of $\mathbf{h}$ means that we are only considering single excitations relative to the reference state $|\text{HF}\rangle$ so we cannot expect to be able to compute excitation energies which refer to doubly excited states of our system. Using the above mentioned approximations, the matrix $(\mathbf{h}|E\hat{I} - \hat{H}(\xi)|\mathbf{h})$, whose evaluation permits us to find the desired poles (and hence excitation energies), becomes

$$\begin{aligned}\mathbf{M} &= \begin{pmatrix} (\mathbf{q}^\dagger|E\hat{I} - \hat{H}(\xi)|\mathbf{q}^\dagger) & (\mathbf{q}^\dagger|E\hat{I} - \hat{H}(\xi)|\mathbf{q}) \\ (\mathbf{q}|E\hat{I} - \hat{H}(\xi)|\mathbf{q}^\dagger) & (\mathbf{q}|E\hat{I} - \hat{H}(\xi)|\mathbf{q}) \end{pmatrix} \\ &\equiv \begin{pmatrix} E\mathbf{1} - \mathbf{A} & -\mathbf{B} \\ -\mathbf{B} & -E\mathbf{1} - \mathbf{A} \end{pmatrix},\end{aligned} \tag{12}$$

where

$$\mathbf{A}=(\mathbf{q}^{\dagger}|\hat{H}(\xi)\mathbf{q}^{\dagger}=(\mathbf{q}|\hat{H}(\xi)|\mathbf{q}), \tag{13}$$

$$\mathbf{B}=(\mathbf{q}^{\dagger}|\hat{H}(\xi)|\mathbf{q})=(\mathbf{q}|\hat{H}(\xi)|\mathbf{q}^{\dagger}), \tag{14}$$

$$(\mathbf{q}^{\dagger}|\mathbf{q}^{\dagger})=(\mathbf{q}|\mathbf{q})=\mathbf{1};\ (\mathbf{q}^{\dagger}|\mathbf{q})=0. \tag{15}$$

Singularities in the inverse of this matrix occur when:

$$\begin{pmatrix} E\mathbf{1}-\mathbf{A} & -B \\ -\mathbf{B} & -E\mathbf{1}-\mathbf{A} \end{pmatrix}\begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix}=\begin{pmatrix} \mathbf{0} \\ \mathbf{0} \end{pmatrix}. \tag{16}$$

The solutions of this (non-Hermitian) eigenvalue problem can alternatively be found by solving a smaller dimensional eigenvalue problem of the form [5]

$$(\mathbf{A}+\mathbf{B})(\mathbf{A}-\mathbf{B})(\mathbf{X}-\mathbf{Y})=E^{2}(\mathbf{X}-\mathbf{Y}). \tag{17}$$

By forming triplet and singlet components of the operators

$$\begin{aligned} q^{\dagger}_{m\alpha}(S)&=(\sqrt{2})^{-1}(m^{\dagger}_{+}\alpha_{+}+m^{\dagger}_{-}\alpha_{-}),\\ q^{\dagger}_{m\alpha}(T)&=(\sqrt{2})^{-1}(m^{\dagger}_{+}a_{+}-m^{\dagger}_{-}\alpha_{-}), \end{aligned} \tag{18}$$

where m, α are orbital indices, and the subscripts label the m_s components of electron spin, we can separate the above eigenvalue proble into separate singlet and triplet problems. By then using the second quantization expression [3] for the complex rotated electronic Hamiltonian, it is possible to obtain explicit formulas for the elements of the requisite **A** and **B** matrices for either (S or T) spin case.

The rotated Hamiltonian, which is nothing but $H(\xi\mathbf{r})$, is written in second quantized form

$$\begin{aligned} H(\xi)=\sum_{rs}[\xi^{2}t_{rs}+\xi V_{rs}(\xi)]r^{\dagger}s \\ +\xi\frac{1}{2}\sum_{rstu}(rs|tu)r^{\dagger}s^{\dagger}ut, \end{aligned} \tag{19}$$

where

$$t_{rs}=\int U_{r}(-\tfrac{1}{2}\nabla^{2})U_{s}\,d\sigma, \tag{20}$$

$$V_{rs}(\xi)=-\int U_{r}\left(\sum_{i}\frac{Z_{i}}{|\mathbf{r}-\mathbf{R}_{i}\xi|}\right)U_{s}\,d\sigma, \tag{21}$$

$$(rs|tu)=\int U_{r}U_{s}\frac{1}{|\mathbf{r}_{1}-\mathbf{r}_{2}|}U_{t}U_{u}\,d\sigma_{1}\,d\sigma_{2}. \tag{22}$$

The spin orbitals $\{U_r\}$ can, at this stage of development, be any orthonormal set. Shortly it will be argued that the $\{U_r\}$ should be the unrotated Hartree–Fock or MC SCF spin orbitals when these approximations are used for the reference state

$|0\rangle$. For future convenience, it is also useful to define

$$h_{rs}(\xi)=\int U_r\left(-\tfrac{1}{2}\nabla^2\xi^2-\sum_i\frac{\xi Z_i}{|\mathbf{r}-\mathbf{R}_i\xi|}\right)U_s\,d\sigma \tag{23}$$

and

$$h_{rs}=h_{rs}(1).$$

Upon substituting the above $H(\xi)$ into Eqs. (13) and (14), one can obtain expressions for the **A** and **B** matrix elements in terms of the t_{rs}, V_{rs}, and $(rs|tu)$ integrals and the reference-state density matrices $\langle 0|r^\dagger s|0\rangle$ and $\langle 0|r^\dagger s^\dagger tu|0\rangle$. As Donnelly and Simons have shown [3], one can develop a computationally straightforward method for implementing this step by introducing a perturbation-like expansion for the reference function $|0\rangle$. As mentioned earlier, $|0\rangle$ should be the "rotated" ground state; that is, $|0\rangle$ should contain rotated orbitals. However in the approach taken here from Ref. 3, $H(\xi)$ is written on a zeroth order part H^0 consisting of the Hartree–Fock Hamiltonian pertaining to the unrotated problem plus a perturbation $V(\xi)$ containing both the usual fluctuation potential and the effects of "rotation" on $H[V(\xi)=H(\xi)-H^0]$. In this case, it is most convenient to choose the unrotated Hartree–Fock orbitals as the set $\{U_r\}$ used to express $H(\xi)$ as in Eq. (19). The elements of the **A** and **B** matrices can then be evaluated correct through first order in $V(\xi)$ to obtain the lowest order correction to the unrotated TDHF propagator.

Alternatively, one could carry out a coordinate rotated SCF calculation to obtain, in a nonperturbative manner, rotated orbitals to use as the $\{U_r\}$. One could then take $|0\rangle$ to be a Hartree–Fock determinant of these rotated orbitals. Although this approach is more satisfactory than that taken here because it avoids the perturbative treatment of the effects of rotation on $|0\rangle$, it is computationally much more demanding since it requires transformation of all one and two electron integrals for every value of θ and α. We feel that we have demonstrated in Ref. 3 the commutational tractability of the perturbative approach put forth here. The resultant first order perturbation based expressions for the singlet ($S=0$) and triplet ($S=1$) components of the rotated **A** matrix defined in Eq. (12) are

$$\begin{aligned}A^{(S,T)}_{m\alpha,n\beta}=\delta_{\alpha\beta}[\xi^2 t_{mn}+\xi V_{mn}(\xi)+\xi(\delta_{mn}\varepsilon_m-h_{mn})]\\ -\delta_{mn}[\xi^2 t_{\beta\alpha}+\xi V_{\beta\alpha}(\xi)+\xi(\delta_{\alpha\beta}\varepsilon_\alpha-h_{\beta\alpha})]\xi(mn|\beta\alpha)+2\xi(1-S)(m\alpha|n\beta),\end{aligned} \tag{24}$$

where we have now chosen to express the complex scaling (ξ) as $\xi=(1/\alpha)\exp(-i\theta)$, which then gives rise, in the Hamiltonian, to

$$t_{rs}(\xi)=\xi^2 t_{rs}. \tag{25}$$

The subscripts $m\alpha$ and $\eta\beta$ refer to the row and column indices of **A**, respectively.

Formulas for the singlet and triplet components of the **B** matrix defined in Eq. (11) are obtained in like manner:

$$B^{(S,T)}_{m\alpha,n\beta}=\xi[(\alpha n|\beta m)-2(1-S)(\alpha m|\beta n)]. \tag{26}$$

In Eqs. (25) and (26), the ε_m are the energies of the unrotated Hartree–Fock orbitals (coming from H^0), and the other integrals appearing are defined in Eqs. (20)–(23). These **A** and **B** matrix expressions reduce, for $\xi=1$, to the usual TDHF matrix elements as given, for example, in Ref. 6.

If, instead of a single determinant reference state, one uses a multiconfigurational reference state (MC–TDHF), the general features outlined above remain the same, but the explicit equations for the **A** and **B** matrix elements change. We still define the excitation operator space in terms of excitations from the reference state

$$\mathbf{h}_2=\{m^{\dagger}\alpha;\alpha^{\dagger}m\}=\{q^{\dagger}_{m\alpha};q_{m\alpha}\}$$

but the occupied and unoccupied orbital labels now refer to a dominant determinant in the MC reference state. The orbitals themselves are, of course, fully consistent MC SCF orbitals for the unrotated problem. In general, a complete operator space can be defined in this way, if we include all higher order (two-particle two-hole, etc.) excitations (see Ref. 7). As in the single-configuration case, we use a perturbative approach [3] to estimate the effects of rotation on the MC reference state. In this case the perturbation $V(\xi)$ is $H(\xi)-H(1)$.

The MC–TDHF version of the above **M** can be expressed in the following manner:

$$\mathbf{M}=\begin{pmatrix} E\mathbf{S}-\mathbf{A} & -\mathbf{B}\\ -\mathbf{B} & -E\mathbf{S}-\mathbf{A}\end{pmatrix}=\begin{pmatrix}\mathbf{S}^{1/2} & \mathbf{0}\\ \mathbf{0} & \mathbf{S}^{1/2}\end{pmatrix}\begin{pmatrix} E\mathbf{1}-\mathbf{A}' & -\mathbf{B}'\\ -\mathbf{B}' & -E\mathbf{1}-\mathbf{A}'\end{pmatrix}\begin{pmatrix}\mathbf{S}^{1/2} & \mathbf{0}\\ \mathbf{0} & \mathbf{S}^{1/2}\end{pmatrix}, \tag{27}$$

where

$$\mathbf{S}=(\mathbf{q}^{\dagger}|\mathbf{q}^{\dagger})\neq 1, \tag{28}$$

$$\mathbf{A}'=\mathbf{S}^{-1/2}\mathbf{A}\mathbf{S}^{-1/2}, \tag{29}$$

$$\mathbf{B}'=\mathbf{S}^{-1/2}\mathbf{B}\mathbf{S}^{-1/2}, \tag{30}$$

and **A** and **B** are defined in Eqs. (13) and (14). Thus in the MC–TDHF approximation, the search for singularities of **M** proceeds in the same fashion as before, with the only difference being that **A′** and **B′** are substituted for **A** and **B**.

To implement such an MC–TDHF treatment, we need to know the **S**, **A**, and **B** matrices. In the expressions given below, the indices refer to spin orbitals rather than to spatial orbitals. Of course, the proper singlet and triplet components can easily be expressed in terms of orbitals using the definition in Eq. (18). The relevant overlap matrix elements are

$$S_{m\alpha,n\beta}=(q^{\dagger}_{m\alpha}|q^{\dagger}_{n\beta})=\delta_{mn}\langle\alpha^{\dagger}\beta\rangle-\delta_{\alpha\beta}\langle n^{\dagger}m\rangle, \tag{31}$$

where the notation $\langle op \rangle$ refers to $\langle o|op|o \rangle$, and $|o\rangle$ is the MC reference state. Likewise, the **A** and **B** matrix elements become

$$\begin{aligned} A_{m\alpha,n\beta}(\xi) = {} & h_{mn}(\xi)\langle \alpha^{\dagger}\beta\rangle + h_{\beta\alpha}(\xi)\langle n^{\dagger}m\rangle \\ & -\sum_{i}[\delta_{\alpha\beta}h_{in}(\xi)\langle i^{\dagger}m\rangle + \delta_{mn}h_{\beta i}(\xi)\langle \alpha^{\dagger}i\rangle] \\ & +\sum_{il}[(i\alpha\|\beta 1)\langle i^{\dagger}n^{\dagger}lm\rangle + (in\|ml)\langle i^{\dagger}\alpha^{\dagger}1\beta\rangle \\ & -(in|1\alpha)\langle i^{\dagger}l^{\dagger}m\beta\rangle - (mi|\beta l)\langle \alpha^{\dagger}n^{\dagger}li\rangle] \\ & \times\sum_{ijl}[\delta_{\alpha\beta}(in|jl) < i^{\dagger}j^{\dagger}lm\rangle + \delta_{mn}(ij|\beta l)\langle i^{\dagger}\alpha^{\dagger}lj\rangle] \end{aligned} \tag{32}$$

and

$$\begin{aligned} B_{m\alpha,n\beta}(\xi) = {} & h_{\alpha n}(\xi)\langle m^{\dagger}\beta\rangle + h_{\beta m}(\xi)\langle n^{\dagger}\alpha\rangle + \xi\sum_{il}[(im\|\beta l)\langle i^{\dagger}n^{\dagger}l\alpha\rangle \\ & +(in\|\alpha l)\langle i^{\dagger}m^{\dagger}l\beta\rangle - (in|lm)\langle i^{\dagger}l^{\dagger}\alpha\beta\rangle - (\alpha i|\beta l)\langle m^{\dagger}n^{\dagger}li\rangle]. \end{aligned} \tag{33}$$

In Eqs. (32) and (33), the summation indices run over all occupied and unoccupied orbitals.

4. Application to Excited States of Li^- and Be

In the calculations discussed here, we are looking for excitation energies E_{ex} which, for some set of rotation parameters (α_0 and θ_0), become relatively independent of α and θ:

$$\left.\frac{\partial E_{ex}}{\partial \alpha}\right|_{\alpha_0} = \left.\frac{\partial E_{ex}}{\partial \theta}\right|_{\theta_0} = 0. \tag{34}$$

If both the ground and excited states are bound, we expect E_{ex} to be independent of α and θ for *all* α, θ. In contrast, if the excited state is metastable, we expect E_{ex} to be independent of θ only for large enough θ (see Ref. 1). In calculations using limited basis sets it will, in general, not be possible to find such a set of parameters. Instead one usually finds that at some values of α and θ, E_{ex} becomes significantly less dependent on α and θ. If one carries out calculations at constant α and varying θ, the points where the "slowing down" occurs are often associated with "kinks" in the graphs of the excitation energies (see, for example, Fig. 1).

In our calculations, the complex resonance energy E_{ex} is taken as the excitation energy at which the maximum slowing down occurs. The real part of this energy gives the energy of the resonance state while the imaginary part gives half the width. In calculating $E_{ex} = E^* - E_0$, we are implicitly *assuming* that the ground-state energy E_0 is fully independent of the rotation parameters α and θ. This is not rigorously the case, and to make it true we would have to perform a *rotated* SCF or MCSCF calculation for each set of values of α and θ to obtain the "rotated" reference state energy. This would, of course, greatly increase the

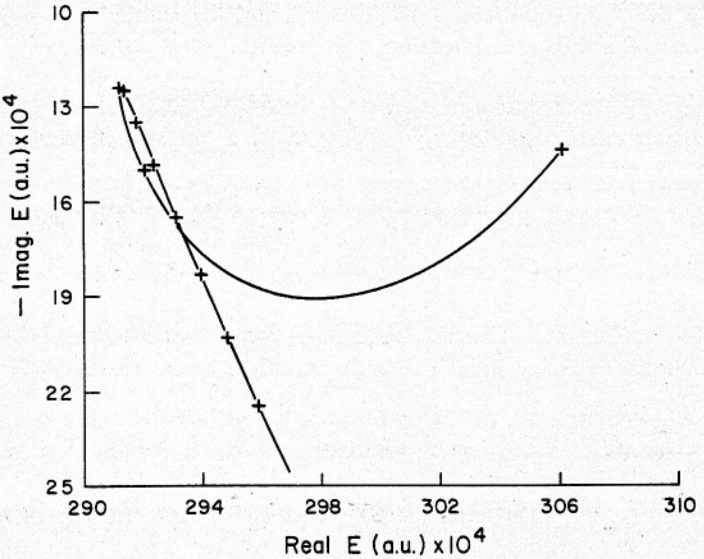

Figure 1. Complex excitation energy for fixed $\alpha = 1.656$ with θ varying from 1.0° (right-hand side) to 10.0° in intervals of 1.0°. Shown here is resonance No. 1 for basis set No. 5.

difficulty and cost of such calculations. Therefore, we have instead chosen to *assume* that the reference state energy E_0 would, even in our finite basis sets, be more θ independent than the resonance excited state which we are interested in studying.

All of the calculations reported here were performed using basis sets consisting of Gaussian-type orbitals (GTO). The first step in each calculation is to perform a Hartree–Fock (SCF) or multiconfigurational Hartree–Fock (MC SCF) calculation to generate a set of molecular orbitals associated with the above mentioned operator space. The reference state is then taken to the converged SCF or MC SCF ground state obtained in this calculation.

$Be(^1S \rightarrow {}^1S, {}^1P)$

In order to test our computer program and to provide estimates of the accuracy to be expected of the method, we carried out a calculation of the $^1S \rightarrow {}^1S$ and $^1S \rightarrow {}^1P$ excitations energies of Be in the absence of any coordinate rotation. The basis set used consisted of $5s$ and $4p$ Gaussian-type orbitals (see Table I), Hand the two configurations used in the MC SCF calculation were $1s^22s^2$ and $1s^22p^2$. The converged CI expansion coefficients obtained in the MC SCF procedure were 0.9515 and −0.1778, respectively.

In Table II we show several of the lowest singlet excitation energies obtained from our calculation together with results of Yeager and Jørgensen [8] and experimental results from Ref. 9. Since our calculations were performed using

TABLE I. Basis set for Be calculation.

	Exponent	Contraction coefficient
1 s	1264.5857	.001945
	189.9368	.014835
	43.1590	.072090
	12.0987	.237154
	3.8063	.469199
	1.2729	.356520
2 s	.7478	1.00000
3 s	.2200	1.00000
4 s	.0823	1.00000
5 s	.0300	1.00000
1 p	3.1965	.055980
	.7478	.261551
	.2200	.793972
2 p	.0500	1.00000
3 p	.0125	1.00000
4 p	.0031	1.00000

Gaussian-type orbitals, where Jørgensen and Yeager used Slater-type orbitals (STO), we cannot expect complete agreement. However, the results in Table II do show satisfactory agreement between the two sets of theoretical numbers. Also, our agreement with the experimental data is good, although not as good as that obtained with the considerably larger STO basis used in Ref. 8. The rather

TABLE II. Lowest singlet excitation energies for Be (in eV.)

Symmetry	experiment[a]	MCTDHF[b]	MCTDHF[c]
2p ^1P	5.28	5.89	6.09
3s ^1S	6.78	6.95	7.79
3p ^1P	7.46	7.69	7.80
4p ^1P	8.33	8.53	8.50
4s ^1S	8.09	8.26	17.66

[a] Experimental results from Ref. 9.
[b] Reference 8.
[c] This work uses basis set shown in Table I.

large discrepancy for the fourth excitation of ^1S symmetry is probably due to our limited basis set which is not designed to yield highly accurate descriptions of orbitals with high principal quantum number.

$Li^-(^1S \rightarrow {}^1P)$

To look for possible excited states of Li$^-$ which are metastable, we performed a single determinant singlet TDHF calculation on ^1S Li$^-$ including in our operator space single excitations $\{\mathbf{q}^\dagger; \mathbf{q}\}$ of p symmetry and using five different basis sets. Based upon the results of e + Li scattering calculations carried out by Moores and Norcross [10], we expect that a resonance state might appear near 0.0301 a.u. (relative the ^2S ground state of Li) with a width approximately equal to the resonance energy. In our preliminary calculations, we scanned the region of α and θ space described by $\alpha \varepsilon [1; 2]$ and $\theta \varepsilon [0; 30]$ deg, and we plotted the complex excitation energies as functions of θ for different values of α. An example of such a graph is shown in Figure 2. Most of the excitation energies plotted in this fashion did not show any stability "kink" behavior but were simply rotated into the fourth quadrant of the complex plane in a manner consistent with scattering state behavior (see Ref. 11). In contrast, certain of the lower lying excitation energies displayed, for specific values of α, trajectories which had a very slow θ dependence once θ reached a critical value. A closer look at these relatively stable trajectories in the neighborhood where the "slowing down" occurs, revealed that for some value of α and θ the rotated excitation energies

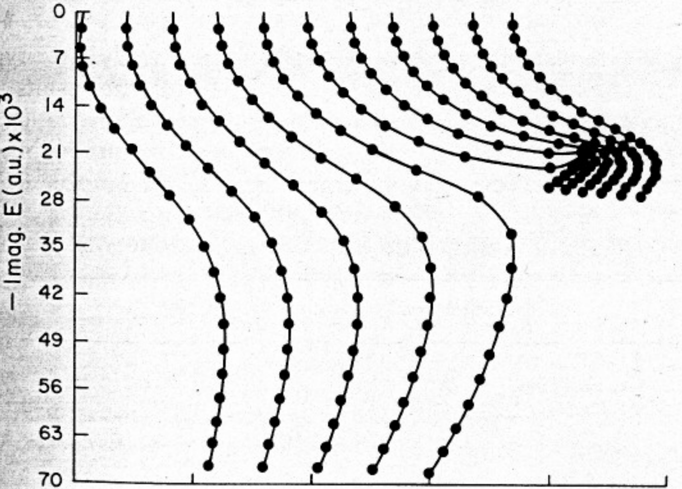

Figure 2. Collection of theta trajectories for the second resonance with α ranging from 1.40 to 1.60 in intervals of 0.02. As the alpha values increase, the trajectories are shifted to the left. The theta values go from 0° to 20° in intervals of 1°. The calculation was performed with basis set No. 5.

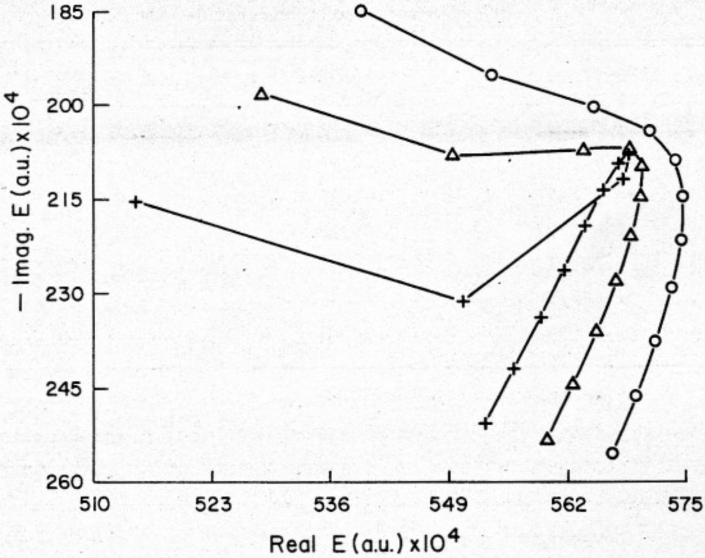

Figure 3. Close view of the "slowing down" region of the second resonance shown in Figure 2. α ranges from 1.46 to 1.50 in intervals of 0.02. The θ trajectories start from the left at theta = 9°, θ increases in steps of 1.0°.

trajectory had the "kink" form shown in Figure 3. For values of θ less than the critical value θ_c (where the "kink" occurs), the behavior of this trajectory was more or less continuumlike, but for larger θ values it slowed down considerably.

The kind of behavior described here is characteristic of all of the results obtained using five different basis sets, although the values of α and θ at which the kink occurred varied from basis to basis. As is shown in Figure 1, the beginning of the "slowing down" occurs close to the tip of the kink. Therefore, we took the value of this complex excitation energy (ΔE) at this stable point to represent the desired complex resonance energy. The real part of ΔE was taken as the *energy* of the resonance state (relative to the *presumed* stable ground state) and the imaginary part as half the resonance *width*.

Within each of the five different basis sets used, we discovered two stable resonance energies when following the above described computational procedure. In Table III we describe our basis sets, and in Table IV we give the real and imaginary parts of the resultant complex resonance energies together with the values of the α and θ parameters at which the resonances were determined for each basis. In Table V we list the excitation energies obtained in the TDHF calculations for each basis.

The scattering calculation on Li^- done by Moores and Norcross in Ref. 8 shows a broad feature near 0.029 a.u. (which they do not attribute to a resonance state of Li^-) with a width of 0.029 a.u. In contrast, our calculations show *two* resonance states lying in this energy range. A narrow resonance with an energy near 0.03 a.u. and a width of 0.003 a.u. and another broader resonance with an

TABLE III. Contracted GTO basis sets 1–5 for Li.

	Exponent	s contraction coefficient	p contraction coefficient
Basis Set No. 1			
1 s	642.41895	.00214	
	96.79849	.01621	
	22.09109	.07732	
	6.20107	.24579	
	1.93512	.47019	
	.63674	.34547	
2 s p	2.19146	.03509	.00894
	.59613	.19123	.14101
	.07455	1.08399	.94535
2 s'p'	.02867	1.00000	1.00000
3 p	.12179		.15559
	.0283		.60768
	.0092		.39196
Basis No. 2 - Same as No. 1 with one p function added			
4 p	.30000		1.00000
Basis No. 3 - Same as No. 2 with one p function added			
5 p	.10000		1.00000
Basis No. 4 - Same as No. 3 with one p function added			
6 p	.80000		1.00000
Basis No. 5 - Same as No. 4 with one p function added			
7 p	.20000		1.00000

energy of approximately 0.057 a.u. and a width of 0.05 a.u. are found. It might be possible to interpret the Moores and Norcross result as consisting of our two "overlapping" states. The lowest one would, in our calculation, correspond to an excitation from the $1s^22s^2$ ground state to $1s^22s2p$ state which then decays by shape resonance tunneling to give $1s^22s$ Li and an electron in a p wave. The broader higher energy resonance corresponds to another shape resonance ($1s^22s3p$) of Li^-. In addition to the broad feature near 0.029 a.u., Moores and

TABLE IV. Results of rotated TDHF calculation on $Li^-(^1P)$.[a]

	First Resonance				Second Resonance			
Basis	ReE	-ImE	alpha	theta (degrees)	ReE	-ImE	alpha	theta (degrees)
1	30.2	3.13	1.84	5	61.4	27.7	1.52	14
2	31.8	1.59	1.67	3	61.6	29.5	1.49	15
3	29.5	1.91	1.69	5	57.3	25.4	1.53	14
4	29.2	1.09	1.66	3	56.1	24.4	1.53	14
5	29.1	1.24	1.66	3	56.8	20.8	1.50	12

[a] All energies are in units of 10^{-3} a.u.

Norcross also studied the sharp "window resonance" which lies just below the $1s^22p$ channel opening. This sharper (Feshbach) resonance, whose electronic configuration is likely to be [11] $1s^22p3s$, could not be investigated in our calculation because it corresponds to a doubly excited configuration relative to our $1s^22s^2$ reference state.

TABLE V. Unrotated ^1P excitation energies for Li^- for basis sets 1–5 (in a.u.).

Basis sets no.				
1	2	3	4	5
.0296	.0294	.0219	.0208	.0206
.0982	.0944	.0889	.0848	.0834
.2047	.1993	.1996	.1828	.1687
2.2367	.6398	.6120	.4261	.3822
2.3333	2.2211	1.1833	.9800	.7437
2.3976	2.3278	2.2208	2.2198	1.5050
	2.3966	2.3205	2.3187	2.2192
	2.7401	2.3931	2.3902	2.3187
		2.7394	2.4854	2.3840
		3.2175	2.5981	2.5705
			3.0659	2.8993
			4.3986	3.0310
				3.5891
				4.9527

In summary, we used a coordinate-rotated version of the TDHF and its multiconfiguration extension to look for metastable excited states of Li^- which are of ^1P symmetry. We found two such resonances, one near 0.06 a.u. with a width of 0.05 a.u. and a second near 0.03 a.u. having a width of 0.003 a.u. The superposition of these two shape resonances could account for the broad structure seen by Moores and Norcross in their $e+\mathrm{Li}$ scattering calculations.

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