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Fully numerical complex-coordinate Hartree-Fock calculations for alkaline-earth resonance states

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A fully numerical multiconfiguration Hartree-Fock program has been modified for performance of calculations on atomic quasibound states using the complex-coordinate (dilation) technique. We present single-configuration calculations for the lowest $^2P^{\circ}$ states of Be^-, Mg^-, Ca^-, Sr^-, and Ba^-, along with results of some small-scale multiconfiguration investigations of the Mg resonance. An instability originating in difficulty satisfying orthogonality constraints prevents a full multiconfiguration treatment of this resonance. Single-configuration dilated Hartree-Fock calculations predict $^2P^{\circ}$ shape resonances for all these systems, though recent extensive calculations show the Ca, Sr, and Ba ions to be bound. Nonetheless, we think it is significant that the dilated numerical method can easily carry out fully variational computations on these heavy atoms, and our results, in conjunction with those of other studies, shed light on the importance of electron correlation in its effect upon the resonance parameters and its variation with progressively heavier alkaline-earth atoms. We also establish the feasibility of accounting for important correlation effects through the use of multiconfiguration approximations, though we have not attempted an accurate calculation in this work. Our Be, Mg, and Ca results agree well with previously published single-configuration dilated basis-set calculations, but no such calculations have been carried out for Sr or Ba. Finally, we investigate the dilational stability of the numerical method since this has been an important consideration in basis-set calculations. A simple exercise based on Cauchy's theorem shows that analyticity of the Hartree-Fock radial wave functions implies that the energy and other physical quantities are independent of the dilation parameter, and a high degree of such independence is demonstrated in our numerical results.

I. INTRODUCTION

The method of complex coordinates (dilation method) has been widely applied in atomic resonance calculations, having been incorporated into several calculational procedures, including the self-consistent field (SCF) technique. In this procedure the complex energy $E_{\text{res}}=\varepsilon-i\gamma/2$, which gives both the position ε (relative to the target energy), and the width γ of the resonance, is calculated self-consistently as the complex eigenvalue of the dilated Hamiltonian. Most dilated SCF applications have been carried out in the basis-set scheme, in which there arise problems attributed to the difficulty of representing highly oscillatory functions with finite-basis expansions. In order to avoid these difficulties, most basis-set calculations are performed using a partially dilated basis set, and, as a result, the computed energies exhibit a significant dependence upon the dilation parameter ϑ. One then uses an auxiliary variational procedure in which the energy calculation is performed over a range of dilation parameters, and the results (the "ϑ trajectory") are analyzed in order to find a stationary point of the energy. This stationary value of the energy is then assumed to give the best approximation to the exact resonance energy. These problems can be avoided in the numerical scheme since it does not rely upon basis-set expansions and since all radial coordinates are dilated. The calculated energies therefore exhibit a high degree of stability in the dilation parameter, as we show here. The feasibility of numerical complex-coordinate calculations and improved dilational stability was first demonstrated by Frye and Armstrong,[1] but it appears that no other dilated numerical SCF studies have been published. Futher development of this approach is reported here.

The formal development of this technique is adequately presented in the literature,[2] so we give only a brief description of it in Sec. II. In Sec. III, the results of our calculations are presented and compared with other published results. The question of analyticity of the solutions and stability in the dilation parameter are treated in Sec. IV, and a summary is given in Sec. V.

II. THE DILATION METHOD

The method of complex coordinates was rigorously formulated in terms of analytic continuation of a unitarily transformed Hamiltonian,[3] but, in practice (and with some loss of generality), one may proceed simply by replacing each radial variable r in the nonrelativistic scattering Hamiltonian with the complex coordinate $z=re^{i\vartheta}$, where $0<\vartheta<\pi/2$ is the dilation parameter. The dilated Hamiltonian resulting from this transformation is non-Hermitian and possesses isolated complex eigenvalues of the Gamow form, $\varepsilon=i\gamma/2$, with $\varepsilon>0$ and $\gamma>0$, corresponding to quasibound resonance states that contain continuum elements but are, remarkably, normalizable. This comes about in the following way. It is well known that the wave functions describing scattering resonances satisfy Siegert boundary conditions,

$$\lim_{r \to \infty} P_{kl} \sim e^{ikr} ,$$

with complex momentum,

$$k = k_R - ik_I, \quad k_R > 0, \; k_I > 0 .$$

Applying the dilation transformation, we have $e^{ikr} \to e^{ikz}$, the argument of the exponential being

$$\begin{aligned} ikz &= ir(k_R - ik_I)(\cos\vartheta + i\sin\vartheta) \\ &= r[i(k_R\cos\vartheta + k_I\sin\vartheta) - (k_R\sin\vartheta - k_I\cos\vartheta)] . \end{aligned}$$

Thus the wave is oscillatory but decays exponentially at large r, provided that ϑ is chosen such that

$$(k_R\sin\vartheta - k_I\cos\vartheta) > 0 .$$

This fact makes possible the application of square-integrable SCF methods to the study of these resonance states. Note that the bound orbitals, which, of course, decay exponentially at large r, are also oscillatory because of the presence of the complex coordinate z in the argument of their exponential damping factors.

Experimentally, resonance states appear as rapid fluctuations in scattering or photoabsorption cross sections and are characterized by a position ε and a width γ, usually considered as parameters of a Breit-Wigner profile for the resonance. In the case of electron-scattering resonances, the resonance position is the energy of the resonance state as measured, usually, from its parent state in the target, and it gives the projectile energy at which the resonance signature appears in the cross section. The resonance width is inversely proportional to the lifetime of the resonance state and gives the width of the resonance signature.

In the standard formulation[2] of the dilated SCF method, the variational principle is applied to an energy functional constructed with the dilated Hamiltonian. It proceeds almost exactly as in the real case (that is, for bound-state systems), and it leads to an analogous set of coupled, complex differential equations for the radial factors in the one-particle spin orbitals. The major difference between the real and complex procedures is that the complex radial functions are not complex conjugated when they appear in inner products. The SCF functions determined in this way yield a stationary, complex energy that approximates the eigenvalue of the dilated Hamiltonian. Since the order relations, *less than* and *greater than,* do not hold in the complex plane, this energy cannot be said to be an extremum, unlike its real (bound-state) counterpart, which gives an upper bound for the eigenvalues.

In the basis-set scheme, the dilated SCF procedure leads, as in the real case, to a Rayleigh-Ritz calculation of the SCF wave functions. In the numerical scheme it leads to dilated Hartree-Fock (HF) equations that differ from the real equations[4] only in that z appears in the place of r, and complex quantities replace real ones. Thus in atomic units (used throughout, unless otherwise noted), the dilated Hartree-Fock equation for the radial function $P_{nl}(z)$ is

$$\frac{d^2P_{nl}(z)}{dz^2} = \left[\frac{\lambda}{z^2} - \frac{2}{z}[Z - Y_{nl}(z)] + \varepsilon_{nl,nl} \right] P_{nl}(z) + \mathcal{G}_{nl}(z) , \tag{1}$$

where $\lambda = l(l+1)$, l being the angular momentum quantum number; Z is the nuclear charge; $Y_{nl}(z)$ is the nuclear screening function; and $\varepsilon_{nl,nl}$ is the (complex) diagonal Lagrange multiplier, which ensures that the radial function $P_{nl}(z)$ satisfies the normalization condition $(P_{nl}, P_{nl}) = 1$. The inhomogeneity $\mathcal{G}_{nl}(z)$ contains the exchange function and terms of the form $\varepsilon_{nl,n'l}P_{n'l}(z)$, where $\varepsilon_{nl,n'l}$ is the (complex) off-diagonal Lagrange multiplier, which ensures satisfaction of the orthogonality condition $(P_{nl}, P_{n'l}) = 0$ in the case of $n' \neq n$. The screening function and the inhomogeneity for P_{nl} depend, in general, upon all the other radial functions, $P_{n'l'}$, so these equations form a coupled system that must be solved iteratively and self-consistently.

In anticipation of obtaining solutions that are holomorphic (i.e., Cauchy analytic) in z, we rewrite the equations in the form

$$\frac{d^2P_{nl}(r;\vartheta)}{dr^2} = \left[\frac{\lambda}{r^2} - \frac{2e^{i\vartheta}}{r}[Z - Y_{nl}(r;\vartheta)] + e^{i2\vartheta}\varepsilon_{nl,nl} \right] \times P_{nl}(r;\vartheta) + G_{nl}(r;\vartheta) , \tag{2}$$

where the new notation indicates that ϑ is considered to be a parameter, and where $G_{nl} = e^{i2\vartheta}\mathcal{G}_{nl}$.

We have solved these equations for atomic scattering resonance systems using an extensively modified version of the multiconfiguration Hartree-Fock code of Fischer.[5] In our single-configuration calculations for the Be and Mg resonances, the starting functions were dilated hydrogenic orbitals. For the heavier systems, the resonance calculation was initiated with dilated functions obtained from a calculation of the targets, the starting function for the resonance orbital being dilated hydrogenic. In the multiconfiguration calculations, the starting functions were taken from earlier results whenever possible, and dilated hydrogenic functions were used otherwise. The boundary conditions to be satisfied by the radial functions (including the resonance orbital) are

$$P_{nl}(0;\vartheta) = 0 \quad \lim_{r \to \infty} P_{nl}(r;\vartheta) = 0 . \tag{3}$$

In practice, however, the second of these boundary conditions must be replaced by a specification of the asymptotic behavior of P_{nl} because the equation is solved only over a finite range of r. Thus for the scattering orbital, some attention must be given to the form of the Siegert boundary conditions appropriate to the resonance system under study

$$\lim_{r \to \infty} P_{nl}(z) \sim \exp^{i[kz - l\pi/2 + (q/k)\ln(2kz) + n_l]} , \tag{4}$$

where k is the (complex) outgoing wave momentum, q is the net charge of the atomic residue, and η_l is the partial-wave phase shift. For all the cases examined below, we have $q=0$.

III. RESULTS FOR THE ALKALINE-EARTH TARGET ATOMS

In dilated SCF calculations, the resonance parameters are determined by subtracting the total SCF energy of the target from the total SCF energy of the resonance state; the result is $\varepsilon - i\gamma/2$. As is well known, HF methods poorly account for electron correlation. Furthermore, the correlation energy is different for the target than for the resonance state. In the dilated Hartree-Fock method, this complicates the determination of the resonance position because of difficulties in balancing correlation in the resonance with that in the target. Since the target and resonance correlation energies are different, they do not completely cancel each other when the subtraction is performed to obtain ε. Correlation balancing does not enter into the determination of the width since the target, being a bound state, has a real energy (zero width).

Since the resonance orbital interacts weakly with all but the outermost target orbitals, we might expect core correlation to cancel, leading to reasonably good single-configuration results. We find, however, that correlation effects are often as large or larger than the resonance parameters we are trying to calculate. Thus it is important that we be able to perform multiconfiguration studies for these systems in order to account for correlation.

In the tables below, we compare our results with those of other dilated SCF calculations, with some results obtained by standard, nondilational, methods, and with available experimental values. Conversions from a.u. to eV were made using 1 a.u. = 27.211 396 eV, and all SCF values are single-configuration results, unless otherwise noted. Our calculations reported in this section were performed with $\vartheta = 0.3$ rad. All of our radial functions are complex-valued functions of r, parametrized by ϑ (in Sec. V we present reasons for supposing that our functions are holomorphic functions of z), and our calculations are fully variational, that is, all radial functions are determined self-consistently.

A. Single-configuration calculations

The alkaline-earth target atoms have closed-subshell configurations ns^2 and the ${}^2P^\circ$ shape resonances are formed when low-energy continuum electrons are captured and retained temporarily in the empty np subshells of these atoms by an angular momentum barrier (see Fig. 1). These temporary negative ions may be described as ns^2np, but we distinguish the resonance orbital from bound orbitals by writing $ns^2\varepsilon p$, where εp denotes a p electron with energy ε in the continuum. These resonances are formed without excitation of the targets, and their parent states are therefore the target ground states. The resonance state decays when the extra electron tunnels through the barrier and escapes to the continuum, leaving the neutral atom in its ground state. This mode of decay is energetically favored because the shape resonance lies above its parent state, usually by a few eV or less. Since the angular momentum barrier is responsible for the temporary retention of the scattering electron, s electrons do not form shape resonances.

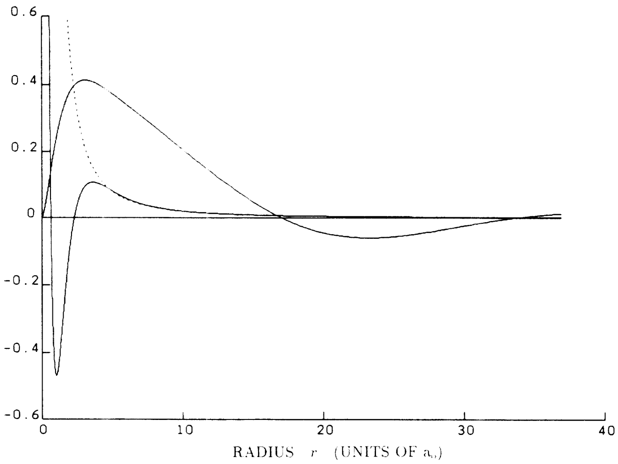

FIG. 1. Real parts of the beryllium resonance function, its effective (direct) potential, and the angular momentum term. The angular momentum term dominates the effective potential at both large and small radius. In particular, it produces an angular momentum barrier in the potential within a few Bohr radii of the nucleus. The vertical axis is marked in atomic units ($a_0^{-1/2}$ for the radial function and a_0^{-2} for the potential and angular momentum curves).

The Be^- ${}^2P^\circ$ shape resonance, which has not been observed experimentally, as far as we know, has been calculated by various theoretical techniques, and selected results from these calculations are given in Table I. An extensive listing of the available data for this resonance has been given recently by Krylstedt *et al.*[6] In Fig. 1 we show the real parts of the normalized resonance function, its effective (direct) potential,

$$U_{\varepsilon p} \equiv \left| \frac{l(l+1)}{r^2} - \frac{2e^{i\vartheta}}{r}[Z - Y_{\varepsilon p}(r;\vartheta)] \right| , \tag{5}$$

and the angular momentum term, $l(l+1)/r^2$, illustrating the origin of the angular momentum barrier.

TABLE I. Results for the Be^- ${}^2P^\circ$ resonance.

Study	Method	ε (eV)	γ (eV)
Present	Numerical dilated HF	0.6879	0.5100
Frye, Armstrong[a]	Numerical dilated HF	0.680	0.490
McNutt, McCurdy[b]	Basis-set dilated HF:		
	single-configuration	0.688	0.510
	configuration interaction	0.323	0.296
Kurtz, Jordan[c]	Phase shift analysis:		
	static exchange (SE)	0.75	1.64
	SE plus polarization	0.14	0.13
Kim, Greene[d]	R matrix plus QDT	0.254	0.206

[a] Reference 1.
[b] Reference 7.
[c] Reference 8.
[d] Reference 9.

The single-configuration approximation for this resonance is $1s^2 2s^2 \varepsilon p$, and our calculation converges to order 10^{-8} (maximum pointwise change in the functions) after 30 iterations. The resonance parameters were determined using the single-configuration Hartree-Fock energy for the neutral beryllium atom, $E_{\text{Be}} = -14.573\,023$ a.u. as the target energy. We obtain this result from a dilated calculation, $\vartheta = 0.3$ rad, of the ground state; the same result is obtained for $\vartheta = 0.0$ (see Table VI).

The close agreement of our result with that of Frye and Armstrong is to be expected since our calculation is essentially the same as theirs (dilated numerical Hartree-Fock), though significant improvements have been made in our program. The agreement with the single-configuration basis-set result of McNutt and McCurdy confirms the adequacy of their basis set for the representation of this resonance. Since rapid oscillations in the asymptotic regions of the core electrons is often cited as a source of difficulty in basis-set calculations, our results are of interest in that regard. In an examination of the normalized $1s$ and $2s$ functions (real parts), we find that the oscillations in the tails are of small amplitude and frequency and are relatively unimportant features (see Fig. 2, where the real parts of the three radial functions are plotted together to display the difference in character and extent of the bound and continuum orbitals). The $2s$ function has only five nodes in the range $8 < r < 60a_0$. The peak amplitude between the first two of these nodes is slightly less than 0.009, and the next maximum is less than 5×10^{-4}. The $1s$ function has only two nodes in the range $1 < r < 5a_0$, and it falls quickly to zero thereafter; the maxima following these two nodes are ~ 0.006 and $\sim 2 \times 10^{-5}$.

For narrow resonances, such as these, correlation effects can be of utmost importance. This fact is suggested by the large effect that the addition of a phenomenological polarization potential has upon the static exchange results of Kurtz and Jordan. The width shows much greater sensitivity to this long-range potential than does the position, and both of them decrease when polarization is included. We note that the static exchange method does not account for relaxation of the core orbitals. This effect, which is accounted for in our fully variational calculation, arises from penetration of the core by the resonance orbital and should increase the depth of the effective potential well for the resonance orbital, thus decreasing the resonance position.

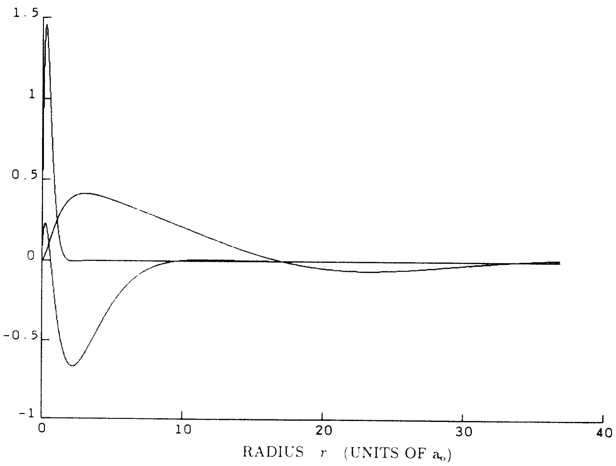

FIG. 2. Real parts of the $1s$, $2s$, and εp radial functions for the beryllium resonance. The vertical axis is marked in units of $a_0^{-1/2}$.

An alternative method of accounting for polarization and other correlation effects is to use multiconfiguration approximations to the wave function in SCF or configuration-interaction (CI) calculations. The Slater-basis CI calculation of McNutt and McCurdy involved 745 configurations including single, double, and triple excitations out of the $2s$ and εp orbitals. Excitations out of the $1s^2$ core were not included. Their CI orbital basis was formed by orthogonalizing Slater functions to orbitals from a (Slater basis) single-configuration SCF calculation of the resonance state and to each other. If we assume that this calculation accounts for most of the electron correlation, then the error in the single-configuration results is about 0.37 eV for the beryllium resonance position and about 0.21 eV for the width. It is remarkable that these errors are as small as they are considering the fact that the single-configuration HF correlation energy for the Be ground state is about 2.62 eV, or about 0.66 eV per electron (see Ref. 10 for the experimental ground state energy).

The Mg^- $^2P^\circ$ shape resonance has been observed experimentally and so provides a test for theoretical methods. The single-configuration wave function is constructed as $3s^2 \varepsilon p\, ^2P^\circ$. Data for this resonance are presented in Table II; a more extensive listing has been given by Krylstedt *et al.*[6] Our results were computed using the single-configuration Hartree-Fock energy for the Mg target, $-199.614\,636$ a.u. The single-configuration approximations, basis-set and numerical, agree well again, and they overestimate both the position and the width. The results of Kurtz and Jordan again demonstrate a high sensitivity to polarization, more pronounced for the width than for the position. Taking the experimental values as accurate, the single-configuration errors are seen to be larger than the resonance parameters themselves: we estimate them at about 0.36 eV for the position and 0.41 eV for the width.

The single-configuration HF approximations, $ns^2 \varepsilon p$,

TABLE II. Results for the Mg^- $^2P^\circ$ resonance.

Study	Method	ε (eV)	γ (eV)
Present	Numerical dilated HF	0.5055	0.5520
McCurdy *et al.*[a]	Basis-set dilated HF:	0.505	0.542
Kurtz, Jordan[b]	Phase shift analysis:		
	Static exchange (SE)	0.46	1.53
	SE plus polarization	0.14	0.24
Kim, Greene[c]	R matrix plus QDT	0.161	0.160
Burrow *et al.*[d]	Experimental	0.15	0.14

[a] Reference 11.
[b] Reference 8.
[c] Reference 9.
[d] Reference 12.

with $n=4,5,6$ for calcium, strontium and barium, respectively, predict shape resonances, and we present our results in Tables III, IV, and V. We have used single-configuration results for the target energies: $-676.758\,186$ a.u. for Ca $-3131.545\,687$ a.u. for Sr, and $-7883.543\,827$ a.u. for Ba. For calcium, basis-set and numerical calculations are again in good agreement. However, recent studies of these heavy alkaline-earth atoms have shown that the lowest $^2P^\circ$ ionic states are bound. In an extensive multiconfiguration calculation supplemented by relativistic corrections, Froese Fischer has determined that Ca^- $4s^24p$, Sr^- $5s^25p$, and Ba^- $6s^26p$ are bound. For calcium, this finding has been corroborated experimentally by Pegg *et al.* and theoretically by the R matrix plus quantum defect theory (QDT) calculation of Kim and Greene, who point to the increasing polarizability of the heavier alkaline-earth atoms to explain the stability of these negative ions. These values have been given as negative in our tabulations since we measure the ion energy relative to that of the neutral atom.

Since single-configuration Hartree-Fock takes no account of correlation effects, our calculations for these highly polarizable systems are not expected to give accurate results. We note, however, that the trend is correct: the position ε drops with increasing atomic number, the downward steps decreasing in size. Our results match those of Kim and Greene within about 26% in this trend, except in the first step, going from Be to Mg, in which case our decrease is twice as large as theirs. Our results for the widths also indicate a strong tendency toward increasing stability (lifetime of the state tending toward infinity).

Because ε is computed by subtracting the resonance energy from the target energy, the errors in our resonance positions largely reflect correlation effects in the outer region of the ionic system. We can estimate the size of these effects and gauge the trend with increasing complexity of the system by comparing our results with those of Kim and Greene. We find that the errors decrease as the targetlike core comes to represent a larger proportion of the total ionic system. For Be and Mg, in which the cores are more strongly affected by the extra electron, the errors are 0.434 and 0.345 eV. In the larger systems the core is better isolated, and the effect of outer correlation is more nearly constant, as one would expect since the outer electron interacts mainly with valence electrons; the errors, in eV, are 0.297 (Ca), 0.287 (Sr), and 0.275 (Ba).

TABLE III. Results for Ca^- $^2P^\circ$.

Study	Method	ε (eV)	γ (eV)
Present	Numerical dilated HF	0.2270	0.1595
McCurdy *et al.*[a]	Basis-set dilated HF:		
	Single-configuration	0.225	0.162
Kurtz, Jordan[b]	Phase shift analysis:		
	Static exchange (SE)	0.24	0.54
	SE plus polarization	0.06	0.10
Fischer[c]	Multiconfiguration HF	−0.062	
Kim, Greene[d]	R matrix plus QDT	−0.070	
Pegg *et al.*[e]	Experimental	−0.043	

[a] Reference 11.
[b] Reference 8.
[c] Reference 13.
[d] Reference 9.
[e] Reference 14.

TABLE IV. Results for Sr^- $^2P^\circ$.

Study	Method	ε (eV)	γ (eV)
Present	Numerical dilated HF	0.1788	0.1140
Fischer[a]	Multiconfiguration HF	−0.106	
Kim, Greene[b]	R matrix plus QDT	−0.108	

[a] Reference 13.
[b] Reference 9.

B. Multiconfiguration investigations

The importance of accounting for correlation effects in resonance states is clear from the results presented above, and we have therefore attempted to develop fully variational multiconfiguration capability with the dilated numerical method. Though we have encountered some difficult problems in this attempt, we believe the results we have obtained in some small-scale calculations are sufficient to demonstrate both the feasibility of this approach and its advantages.

In the construction of a multiconfiguration wave function for the magnesium resonance, we examined low-lying configurations that represent important correlation effects. Such effects represented by $s-d$ replacements are often large; accordingly, we added to the reference configuration, $3s^2\varepsilon p$, the configuration state $3s3d(^3D)\varepsilon p$, which was found to be important in Fischer's investigation[12] of Mg^-. This addition takes partial account of the polarization of the $3s$ valence orbitals by introducing higher multipole interactions into the coupling of the resonance orbital with the target, but it introduces no additional orthogonality constraints involving the resonance orbital. Its inclusion in the wave function produces a dramatic reduction in both the width and the position, having a much larger effect on the width. Such an effect might be anticipated on the basis of the results of Kurtz and Jordan, mentioned above. The two-configuration results are $\varepsilon=0.311$ eV and $\gamma=0.073$ eV. The configuration mixing coefficients, which are complex,

TABLE V. Results for Ba^- $^2P^\circ$.

Study	Method	ε (eV)	γ (eV)
Present	Numerical dilated HF	0.0985	0.0336
Fischer[a]	Multiconfiguration HF	−0.148	
Kim, Greene[b]	R matrix plus QDT	−0.176	

[a] Reference 13.
[b] Reference 9.

were calculated self-consistently as $3s^2\varepsilon p$: (0.986, 0.006) and $3s3d(^3D)\varepsilon p$: (0.172, −0.034).

It is important to note that addition of terms to the resonance wave function tends to produce decreases in the position, but their effects upon the width are not predictable: the width varies nonmonotonically with the addition of new configurations. These tendencies, which may also be seen in the CI calculation of McNutt and McCurdy,[7] and in dilated numerical multiconfiguration studies on a lithium resonance,[15] suggest that the SCF result for the position—but not the width—is an upper bound; however, this has not been demonstrated theoretically.

We then added a third configuration state $4s^2\varepsilon p$, which introduces no orthogonality constraints involving the εp orbital. At convergence we obtain $\varepsilon=0.236$ eV and $\gamma=0.030$ eV, the new configuration mixing at only (−0.074,0.004), thus its effect upon the resonance parameters is insignificant.

Because the $3p^2(^1S)$ configuration is important in accounting for interelectron repulsion between the $3s$ electrons in the target expansion, it is expected to play an important role in the ion as well. In addition to $3p^2(^1S)\varepsilon p$, the ^1D and ^3P terms of $3p^2$ can also contribute to the resonance, though not to the target. Normally, the $3p$ and εp orbitals would be required to satisfy an orthogonality relation, but we have found that this constraint introduces an intractable instability in the Mg case. A four-configuration calculation including the reference configuration and all three intermediate couplings of $3p^2$ converges well if the orthogonality constraint is dropped. Because of unbalanced correlation, the resonance energy drops below that of the single-configuration target energy. Thus we switch to the two-configuration $(3s^2+3p^2\,^1S)$ Hartree-Fock value for the target energy, −199.646 074 a.u.; the resulting resonance parameters are $\varepsilon=0.484$ eV and $\gamma=0.206$ eV. The configuration mixing coefficients are found to be (0.939, 0.032) for $3s^2\varepsilon p$ and (0.340, −0.070), (0.048, −0.013), and (0.098, −0.054) for the ^1S, ^1D, and ^3P intermediate couplings, respectively, of $3p^2\varepsilon p$. The (complex) overlap of the $3p$ and εp functions is quite large upon convergence: $(P_{3p},P_{\varepsilon p})=(0.95,\ -0.19)$. The $3p$ orbital sits inside the εp orbital, their average radii (real parts only) in units of the Bohr radius being $3.9a_0$ and $5.3a_0$. When orthogonality is required, the εp orbital tends to become extremely diffuse, its average radius reaching into the thousands of Bohr radii, and the calculation becomes unstable, failing to converge.

We suspect that this difficulty with orthogonality appears in this case because the constraint applies to a virtual orbital in a configuration of major importance, while the role to be played by that orbital in the resonance system is not so easily determined as in the target. In an expansion of the target wave function, the $3p$ virtual orbital represents the effects of correlation upon the $3s$ valence electrons and has an average radius of about $3.0a_o$, that of the $3s$ orbitals being about $3.2a_o$. The role to be played by the $3p$ orbital in the resonance is difficult to predict, since the resonance orbital itself is, nominally, a $3p$, and the $3p^2\varepsilon p$ configuration may represent virtual excitations of the valence electrons into the resonance orbital. Inclusion of configurations such as $3p^3$ and εp^3 along with $3p^2\varepsilon p$ in an attempt to define better the roles of the two orbitals did not improve the stability sufficiently for convergence. Various attempts were also made, without success, to introduce a $3p$ orbital that would represent inner correlation (that is, for the valence orbitals, as in the target expansion) and a $3p'$ or $4p$ orbital that would represent outer correlation (that is, for the diffuse part of the wave function).

We have found that the lithium resonance, $1s^2 2s\varepsilon p\ ^3P^\circ$, is not susceptible to this problem, probably because the $2s2p^2\varepsilon p$ configuration states mix much less strongly (∼0.04 for the ^1S coupling, which is the largest contributor) than in the magnesium case. In the lithium resonance, the $2p$ virtual orbitals are highly contracted, representing inner correlation, lying only slightly beyond the $1s$ orbitals. If the orthogonality constraint is dropped, the $2p$ orbitals contract slightly but remain outside the $1s$ shell.

The error introduced by ignoring orthogonality is also difficult to estimate. Our only clue comes from the lithium case, in which dropping the orthogonality constraint causes a decrease in both ε and γ; the decrease is $\mathcal{O}(10^{-3})$, an order of magnitude smaller than the mixing coefficient of the added configuration.

IV. ANALYTICITY AND STABILITY

It is shown in the rigorous formulation of the dilation method[3] that the discrete eigenvalues, both real and complex, of the dilated Hamiltonian are independent of the dilation parameter (within some bounds that need not concern us, here). In this section we give the essential elements of a demonstration that analyticity of the SCF radial functions implies stability of the energy (and other physical quantities) in the dilation parameter ϑ. This fact has long been recognized, but we are aware of no demonstration of it in the literature. We follow the proof with an examination of the ϑ stability of our energy calculations. It is our contention that numerical integration of the dilated Hartree-Fock equations produces radial functions that are nearly exact solutions of the coupled differential equations and that are holomorphic in the complex coordinate z though we do not attempt a verification of this, here. The high degree of dilational stability exhibited by our results does not prove that our solutions are holomorphic, but it strongly suggests as much. In contrast, the functions used in partially dilated basis-set calculations are not holomorphic in z, and, consequently, resonance energies calculated with such bases exhibit substantial dilational nonstability.

The proof of dilational stability makes use of simple properties of holomorphic functions, and thus is quite general. We state it here in a form that is directly applicable to the present considerations. We assume that a function, $f(z)$ is holomorphic on some domain, $\mathcal{D}$ containing the contour C which is the line segment $z=re^{i\vartheta}$ with $0\le r\le R$, for some $R>0$ and $\vartheta>0$. Then the derivative of $f(z)$ exists and is continuous on C, as are the partial derivatives of f with respect to r and ϑ. Furthermore, the Cauchy-Riemann equations are satisfied, and it follows that

$$\frac{df}{dz}=e^{-i\vartheta}\frac{\partial f}{\partial r}=\frac{e^{-i\vartheta}}{ir}\frac{\partial f}{\partial\vartheta} .$$

Now we form the integral

$$I=\int_C dz\frac{df}{dz}=f(Re^{i\vartheta})-f(0) ,$$

and use the relations above to express it as

$$I=\int_0^R dr\frac{\partial f}{\partial r}=-i\int_0^R dr\frac{1}{r}\frac{\partial f}{\partial\vartheta} .$$

In the last integral, ϑ appears as a parameter, and we can interchange the order of integration and differentiation to obtain

$$I=-i\frac{\partial}{\partial\vartheta}\int_0^R dr\frac{1}{r}f(r;\vartheta) .$$

From this result we see that, if $I=f(R;\vartheta)-f(0)=0$, then

$$\frac{\partial}{\partial\vartheta}\int_0^R dr\frac{1}{r}f(r;\vartheta)=0 .$$

For present purposes, we extend the range of r to $(0\leq r\leq\infty)$ under the additional assumption that $\lim_{R\to\infty}f(R;\vartheta)<\infty$, and that the improper integrals exist. Under the stated assumptions, we have proved, then, that $[f(0)-\lim_{R\to\infty}f(R;\vartheta)]=0$ implies that the integral, $\int_0^\infty dr(1/r)f(r;\vartheta)$ is independent of ϑ.

In the dilated HF method, physical quantities such as the total kinetic and potential energy and the "single-particle energies" (the diagonal energy parameters), are calculated as sums of integrals of the form

$$\int_0^\infty dz\int_0^\infty dz' P_i(z)P_j(z')\mathcal{O}P_s(z)P_t(z') ,$$

where $\mathcal{O}$ is a differential or multiplicative operator. These integrals and their integrands can easily be shown (case by case) to reduce to forms that satisfy the requirements of our theorem, provided that the radial functions are holomorphic on a domain containing the half-line of integration, vanish at the origin, and decay sufficiently rapidly as $r\to\infty$. The boundary conditions imposed upon the solutions of the dilated HF equations [see Eq. (3)] ensure the satisfaction of the last two requirements for the bound as well as the resonance orbitals. We have the result that dilational stability of the energy and other physical quantities is a necessary, but not sufficient, condition for analyticity of the radial functions.

The mathematical content of this development is just that of Cauchy's integral theorem specialized for our purposes: since the integrand is holomorphic and vanishes at infinity in $\mathcal{D}$, integration around a closed contour consisting of two rays $re^{i\vartheta_1}$ and $re^{i\vartheta_2}$, plus an arc at infinity, will give zero, provided that the contour lies completely within $\mathcal{D}$. Since the integration over the arc contributes nothing, it follows that the integrations over the two rays must cancel, and ϑ independence of the integral is thus established. As Junker has remarked,[16] even a crude approximation to the wave function will yield dilationally stable results if the function is holomorphic in z. In the tables below, we demonstrate the dilational stability of our calculated energies for the Be bound-state and shape resonance.

TABLE VII. ϑ stability of the Be$^-$ $1s^2 2s^2 \varepsilon p\ ^2P^\circ$ energy.

ϑ (rad)	ReE (a.u.)	ImE (a.u.)
0.05	−14.547 743 686 110 804	−0.009 370 180 477 076
0.10	−14.547 743 686 093 196	−0.009 370 180 860 578
0.20	−14.547 743 685 902 339	−0.009 370 181 617 102
0.30	−14.547 743 685 528 850	−0.009 370 182 302 109
0.40	−14.547 743 685 023 610	−0.009 370 182 876 527
0.50	−14.547 743 684 437 183	−0.009 370 183 339 561
0.60	−14.547 743 683 793 517	−0.009 370 183 719 235
0.70	−14.547 743 683 075 353	−0.009 370 184 049 253
0.80	−14.547 743 682 228 870	−0.009 370 184 325 789
0.90	−14.547 743 681 183 459	−0.009 370 184 500 227
1.00	−14.547 743 679 905 232	−0.009 370 184 450 735
1.10	−14.547 743 678 396 239	−0.009 370 184 001 181
1.15	−14.547 743 677 248 913	−0.009 370 183 184 738

From these tables (see, for example, Table VI, right-hand column) one can clearly see evidence of a small error that varies with ϑ. This error is far too small to affect our results for the resonance parameters, and we may ignore it.

As noted in earlier sections, we have calculated single-configuration target energies using $\vartheta=0.3$. It is clear from the results given in Table VI that ordinary Hartree-Fock energies could have been used just as well. Our $0\leq\vartheta\leq 0.6$ rad results for Be, for example, reproduce the real Hartree-Fock result through at least six decimal places (cf. Ref. 4, p. 28).

As ϑ is increased, convergence is more difficult to achieve. In Table VII, the results for angles greater than 0.7 rad are set off from the others as an indication that those sets were run using starting functions from the $\vartheta=0.7$ rad set (which converges from dilated hydrogenic starting functions, as do the sets at the smaller angles) and working up to larger angles.

V. SUMMARY

In this paper we have reported further development of a fully numerical dilated Hartree-Fock method for the investigation of atomic resonance states, after the feasibility

TABLE VI. ϑ stability of the Be $1s^2 2s^2$ energy.

ϑ (rad)	ReE (a.u.)	ImE (a.u.)
0.00	−14.573 023 171 519 479	0.000 000 000 000 000
0.10	−14.573 023 171 473 565	−0.000 000 000 583 754
0.20	−14.573 023 171 346 417	−0.000 000 001 145 013
0.30	−14.573 023 171 162 906	−0.000 000 001 678 996
0.40	−14.573 023 170 943 826	−0.000 000 002 207 723
0.50	−14.573 023 170 683 654	−0.000 000 002 774 518
0.60	−14.573 023 170 333 851	−0.000 000 003 423 363

of this type of calculation was demonstrated by Frye and Armstrong.[1] Correlation error is inherent in any Hartree-Fock calculation so we expect single-configuration results to be inadequate if correlation effects are large; we have estimated the errors in our resonance parameters as being less than 0.5 eV, but this error is of the same order as the parameters themselves. Thus multiconfiguration capability is required so that correlation effects may be accounted for.

Although instabilities originating in an orthogonality requirement have prevented a full multiconfiguration development of the Mg resonance, our small-scale multiconfiguration calculations demonstrate the feasibility and effectiveness of dilated numerical multiconfiguration studies as a means of accounting for electron correlation, this being particularly important for narrow resonances in polarizable targets. Aside from the instability that is encountered in this case, these fully variational numerical multiconfiguration calculations can be performed with little more difficulty than in ordinary nondilated Hartree-Fock calculations, giving well-known advantages over dilated CI calculations. The lowest $^3P^\circ$ shape resonance of Li^- is not susceptible to this instability, and an extensive multiconfiguration treatment of that system is currently in progress.

With the numerical method we have avoided some of the difficulties met in calculations using partially dilated basis sets. In particular, we have demonstrated a high degree of dilational stability, thus eliminating the need to undertake the construction of a ϑ trajectory for the energy and a search for a stationary point on it. We can perform such numerical calculations using simple starting functions, and we avoid the problem of choosing and optimizing a basis set. We have shown that analyticity of the SCF radial functions implies such dilational stability, supporting our supposition that our functions are holomorphic.

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[1] D. Frye and L. Armstrong, Jr., Phys. Rev. A **34**, 1682 (1986).

[2] See, for example, various papers in Int. J. Quant. Phys. **14**, (4) (1978). For treatment of the dilated SCF technique, see, for example, B. R. Junker, in *Autoionization: Recent Developments and Applications,* edited by A. Temkin (Plenum, New York, 1985); Adv. At. Mol. Phys. **18**, 207 (1982); and for a development specific to the numerical approach see M. Bentley, Ph.D. dissertation, John Hopkins University, 1989.

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

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

[5] C. Froese Fischer, Comput. Phys. Commun. **14**, 145 (1978).

[6] P. Krylstedt, M. Rittby, N. Elander, and E. Brändas, J. Phys. B **20**, 1295 (1987).

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

[8] H. A. Kurtz and K. D. Jordan, J. Phys. B **14**, 4361 (1981).

[9] L. Kim and C. H. Greene, J. Phys. B **22**, 1175 (1989).

[10] C. F. Bunge, Phys. Rev. A **14**, 1965 (1976).

[11] C. W. McCurdy, J. G. Lauderdale, and R. C. Mowrey, J. Chem. Phys. **75**, 1835 (1981).

[12] P. D. Burrow, J. A. Michejda, and J. Comer, J. Phys. B **9**, 3225 (1976).

[13] C. Froese Fischer, Phys. Rev. A **39**, 963 (1989).

[14] D. J. Pegg, J. S. Thompson, R. N. Compton, and G. D. Alton, Phys. Rev. Lett. **59**, 2267 (1987).

[15] M. Bentley (unpublished).

[16] B. R. Junker, in *Autoionization: Recent Developments and Applications* (Ref. 2), p. 116.