

# Coordinate Rotation Studies of $H^-$ , $He^-$ , $Be^-$ , $Mg^-$ Resonances: Basis Set and Configuration List Dependence

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## Abstract

We have performed coordinate rotated configuration interaction calculations on well-studied Feshbach resonances of  $H^-$  and  $He^-$  and on  $^2P$  shape resonances of  $Be^-$  and  $Mg^-$ . The focus of our efforts was the dependence of computed resonance energies on both the quality of the atomic-orbital basis and the level of treatment of electron correlation. Our results indicate that great care must be taken to guarantee that a basis is adequate; commonly used quantum-chemistry bases are probably far from satisfactory. Our findings also indicate that a proper treatment of inner-shell orbitals within coordinate rotation calculations is a formidable task. We are therefore encouraged to look carefully for modified coordinate rotation techniques that focus on the active valence-level orbitals and may avoid spurious complex energies arising from improper treatment of inner shells.

## 1. Introduction

In recent years, the complex-scaled Hamiltonian (sometimes called "coordinate rotation" or CR) method has become accepted as a useful tool for the study of metastable states of atomic and molecular systems [1]. Many studies have involved electron-atom scattering systems, with one- or two-electron target atoms. Many-electron targets present no formal difficulties; computationally, however, they are formidable problems for which several modified CR procedures have been proposed [2,3]. Most of these new procedures involve assumptions above and beyond those contained in the originally proposed complex scaling procedure.

The purpose of this paper is to re-explore the CR method in two variations: as originally proposed and using an intuitively reasonable modification introduced here. We desire to see if application of these methods to small test systems [using standard quantum-chemistry basis sets within small configuration interaction (CI) calculations] gives reasonably accurate results. Our test systems are the  $^2S$  resonances of  $H^-$  (near 9.56 eV) and  $He^-$  (near 19.4 eV). These resonances have been studied by other researchers using a variety of methods (including CR and experiment), so the correct resonance energies are well known [3].

Section 2 gives a brief overview of the CR method, and defines the "original CR" (OCR) method as well as a new variation whose use we explored on  $H^-$ ,

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He<sup>-</sup>, and on many-electron cases Be<sup>-</sup> and Mg<sup>-</sup>. Section 3 gives the details of our calculations, including basis sets, orbitals, and configuration lists. Section 4 gives the results we obtained for our test problems and in Sec. 5 we discuss the outlook for the methods of this paper.

## 2. Survey of the CR Method

### A. Overview of Basic Coordinate Rotation Theory

The original papers on the method of complex scaling of the Hamiltonian are due to Aguilar, Balslev, Combes, and Simon [4]. More pedestrian summaries of the technique have been given by several authors [5]. The following is a survey of the *results* of the original theorems. Since molecular systems introduce new formal and practical complications, the development below is restricted to atomic targets. The method outlined below, which we refer to as the OCR method, has been used previously by other workers [6]. Whether or not it is the most appropriate CR technique is part of what this research attempts to answer. Certainly it is one of the most straightforward ways to implement CR.

In the OCR method, one begins by taking an atomic Hamiltonian,

$$\begin{aligned}
 H &= -\frac{1}{2} \sum_j \nabla_j^2 - \sum_j \frac{Z}{r_j} + \frac{1}{2} \sum_{j \neq k} \frac{1}{|r_j - r_k|} \\
 &= T + V = T(1) + V(1),
 \end{aligned}
 \tag{1}$$

and scaling the *lengths* of the coordinates of *all* the electrons by an arbitrary complex parameter,  $\eta = \alpha \exp(i\theta)$ . Since the kinetic energy  $T$  and Coulombic potential energy  $V$  scale analytically with  $\eta$ , the effect of the scaling is to form  $T(\eta) = T(1)/\eta^2$  and  $V(\eta) = V(1)/\eta$ . ( $\eta = 1$  corresponds to the unscaled situation.) The spectrum of this scaled Hamiltonian,  $H(\eta)$ , is related to the spectrum of  $H(1)$  as follows.

Any *bound-state* energies of the spectrum of the anion system are invariant to the choice of  $\eta$  provided  $\theta$  is less than  $\pi/2$ . From each target atom (the system with one fewer electron) bound-state threshold (i.e.,  $E = -0.500, -0.125, -0.05556$  a.u., etc., for an H atom), there is a continuous set of *scattering-state* energies lying on the ray emanating from that threshold and making an angle of  $-\theta$  with respect to the real axis (see Fig. 1). Finally, any *metastable state* of the anion system [corresponding to a complex energy, with the imaginary part of the energy being related to the width ( $\Gamma$ ) of the resonance] behaves like a scattering state, until  $2\theta$  is large enough so that the ray from the proper threshold of the target "uncovers" the resonance (see Fig. 1). For  $\theta$  larger than this "critical  $\theta$ ," resonances behave like bound states in that their energies remain unchanged as  $\theta$  further varies (unless  $\theta$  gets *too* large; then the resonance is "covered up" again by the ray of scattering states emanating from the next higher threshold). The eigenfunction corresponding to this resonance is square integrable for  $\theta > \theta_{\text{crit}}$  and, as such, can be described by a square integrable ( $L^2$ ) basis set.

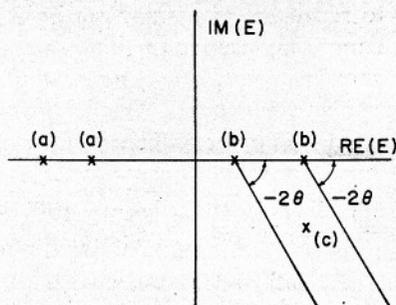


Figure 1. Variation of bound (a), continuum (rays), and resonance (c) state energies with rotation angle  $\theta$ . Points (b) label target thresholds.

### B. Nonideal Behavior—The Core-Electron Problem

In any finite basis the behavior described in the above paragraph is only approximated. In particular, bound-state energies are not totally invariant with respect to  $\eta$ , scattering states do not lie exactly on rays emanating from the target thresholds, and resonances do not show perfect "critical  $\theta$ " behavior.

The source of part of this nonideal behavior can be seen by noting that, according to the CR theorems, the *energies* of bound states are invariant with respect to the state parameter, but the *wave functions* themselves are not. This has been explicitly demonstrated by Junker and Huang for hydrogenic atoms, for which the CR results can be obtained in closed form [7]. The energy levels are still  $-Z^2/(2n^2)$ , but the wave functions are the hydrogenic wave functions *but* with  $r$  replaced by  $r\eta$ . For any atom, the small- $r_i$  dependence of the Hamiltonian is dominated by the terms  $-\frac{1}{2}\nabla_i^2 - Z/r_i$ . Hence if we write the small- $r_i$  behavior of the  $N$ -electron wave function as an antisymmetrized ( $A_N$ ) product involving an  $r_i$ -dependent term  $\phi$  and the remaining part  $\chi$

$$\psi(r_1 \cdots r_i \cdots r_N) \cong A_N[\phi(r_i)\chi(r_x)] \quad (x = 1, 2, \dots, i-1, i+1, \dots, N), \quad (2)$$

then for small  $r$ ,

$$\phi(r) = R_{nl}(r) \exp(-Zr/na_0) Y_{lm}(\theta, \phi), \quad (3)$$

where  $R_{nl}$  is the usual hydrogenic radial function. When we scale the Hamiltonian, clearly we obtain

$$\phi_\eta(r) = R_{nl}(r\eta) \exp(-Zr\eta/na_0) Y_{lm}(\theta, \phi) \quad (4)$$

as the corresponding small- $r$  part of the eigenfunction of  $H_\eta(r) = H(\eta r)$ . This function can be rewritten

$$\phi_\eta = R_{nl}(r\eta) \exp[-a\alpha r \cos(\theta)] \exp[-ia\alpha \sin(\theta)r] Y_{lm}(\theta, \phi), \quad (5)$$

where the real ( $\alpha$ ) and imaginary [ $\exp(i\theta)$ ] parts of  $\eta$  have been introduced and the factor "a" incorporates several constants. We see that scaling not only changes the radial size of  $\phi$ , but also introduces an oscillatory behavior. Such

oscillations are difficult to represent in a small set of Gaussian or Slater basis functions [8] such as are commonly used in *ab initio* quantum calculations. Since the "a" in Eq. (5) is proportional to  $Z$  (and hence the electron number), this problem is worse for many-electron systems. That is, proper treatment of rotated "core" orbitals becomes more and more difficult as the nuclear charge increases. Clearly such oscillatory behavior which occurs in  $\psi_n$  is qualitatively different from the  $r$  dependence appearing in the unscaled wave function. Hence using the usual (unscaled) Hartree-Fock orbitals  $\{\phi_i(r)\}$  as a *basis* to describe the low-lying core electrons

$$\phi_n(r) = \sum_i C_i(\eta) \phi_i(r), \quad (6)$$

in a CR calculation could introduce *spurious* variation of the energy expectation value of  $\psi_n$  as  $\eta$  is varied. The rather smooth unscaled Hartree-Fock orbitals simply cannot describe the highly oscillating rotated core part of  $\psi_n$ . As we indicate below, this "core-electron problem" is very difficult to treat in conventional quantum-chemistry methodology.

### C. Attempts to Circumvent the Core-Electron Problem

From the above, it is clear that low-energy molecular orbitals pick up the most oscillatory behavior under CR. The core electrons, on the other hand, are those expected to be the *least* important as far as the scattering physics giving rise to the temporary anion is concerned (except for core-excited Auger resonances). One would therefore often like to treat the core as passively as possible. However, to keep the energy expectation value from varying wildly (spuriously) with  $\eta$ , it appears that the core needs to be treated the *best*. There have been some attempts made to circumvent this core-electron problem, a few of which we now mention.

Rescigno, McCurdy, and Orel [8] have suggested that one employ antisymmetrized ( $A_{N+1}$ ) ( $N+1$ )-electron basis functions  $\{\chi_i\}$  in which the radial coordinate of only *one* "active" orbital  $\phi_i$  is rotated

$$\chi_i = A_{N+1}[\psi_0(\mathbf{r}_1 \cdots \mathbf{r}_N) e^{-i\theta/2} \phi_i(r e^{-i\theta})]. \quad (7)$$

In effect, the core electrons (orbitals) are simply not coordinate rotated. To then form the complex matrix representative of the unscaled electronic Hamiltonian  $\langle \chi_i | H | \chi_j \rangle$  would require calculation of one- and two-electron integrals involving the real basis functions appearing in  $\psi_0$  and the complex orbitals  $\phi_i(r e^{-i\theta})$  for each value of the rotation angle  $\theta$ . To avoid this computational problem, they further approximated  $H$  by its finite projection onto a set of *real* ( $N+1$ )-electron configurations  $\{\chi'_k\}$  so as to replace the above matrix elements by

$$\langle \chi_i | H | \chi_j \rangle \cong \sum_{k,l} \langle \chi_i | \chi'_k \rangle \langle \chi'_k | H | \chi'_l \rangle \langle \chi'_l | \chi_j \rangle. \quad (8)$$

As a result, they only need to compute overlap integrals arising in  $\langle \chi_i | \chi'_k \rangle$  as  $\theta$  varies. This final approximation to  $\langle \chi_i | H | \chi_j \rangle$  is then used as the rotated Hamil-

tonian matrix from which bound, scattering, and resonance eigenvalues are obtained.

Junker and Huang (JH) [7] have introduced a similar idea for focusing on one active orbital. They use a coordinate rotated Hamiltonian operator  $H_\eta$  but they append to their *real* atomic-orbital basis [from which  $(N+1)$ -electron configurations are eventually constructed] a rotated basis function whose radial form involves  $\exp(-\gamma r e^{i\theta})$ . The molecular orbitals formed from this augmented atomic basis therefore contain some component (determined by the stationary principle used by JH) of this "continuum" orbital. To form the Hamiltonian matrix elements needed to perform the JH calculations, one needs to compute the one- and two-electron integrals over the augmented basis as the rotation angle  $\theta$  is varied.

Donnelly and Simons [9], Winkler and Yaris [9], and Mishra, Froelich, and Öhrn [9] have made use of the coordinate rotation method within the framework of the one-electron Green's function (GF). This GF provides, through the order in electron-electron interaction for which it is computed, the effective interaction potential which the  $(N+1)$ st electron feels due to the  $N$  other electrons and the atom's nucleus. By coordinate rotating this nonlocal one-electron effective potential, the above workers are also able to concentrate on the active electron and to sidestep the core-electron problem.

Each of the methods mentioned above has its own strengths and weaknesses. It is not our purpose here to critically evaluate each such method. Rather, we are attempting to address only the straightforward implementation of the CR method at the  $(N+1)$ -electron level in which the rotated Hamiltonian  $H_\eta$  is diagonalized within a basis of *real*  $(N+1)$ -electron configuration functions. As we shall see later, the rather pessimistic outlook for straightforward CR calculations lends support to the types of alternative approaches outlined above.

#### D. The Subtracted Core Technique

What is *desired* is a procedure which: (i) allows one to treat the "core" electrons passively without completely excluding them from the calculations; (ii) does not require recalculating integrals and overlap matrices for every value of  $\eta$ ; (iii) requires only minor modifications to existing quantum-chemistry computer programs, and (iv) gives good results for reasonable basis sets and within commonly used treatment of electron correlation. It has been suggested [8] that full-CI calculations with large basis sets would be necessary to adequately describe the rotated cores of many-electron atoms. Hence we pose the question: is it possible to *subtract off* the (perhaps poorly described) effect of rotation on the core and thereby focus on the active orbital space only?

With this in mind, we now consider what we refer to as the "subtracted CR" (SCR) method (the "intuitively reasonable" modification referred to in Sec. 1). Instead of looking for a critical value of  $\theta$  with a subsequently stationary eigenvalue of the  $(N+1)$ -electron Hamiltonian, we look for critical behavior in the energy difference  $E_\eta(N+1) - E_\eta(N)$ . Here,  $E_\eta(N+1)$  and  $E_\eta(N)$  are the

eigenvalues of the *scaled*  $(N+1)$ - and *scaled*  $N$ -electron Hamiltonians, respectively. In a complete basis,  $E_\eta(N)$  would be a real *constant* (independent of  $\eta$ ) equal to the  $N$ -electron ground-state energy of the bound target atom. Within a finite basis, it seems probable that the cores of the  $(N+1)$ - and  $(N)$ -electron systems would both pick up about the same amount of "spurious" energy variation as  $\eta$  is varied. This *assumption* forms the basis of the SCR method. In this paper we view the SCR as a numerical experiment, without trying to give it further theoretical justification.

In evaluating the OCR, SCR, or any other proposed technique, two important questions still remain. The first deals with the choice of an atomic-orbital basis. In this study, for each test metastable anion, we used several basis sets of increasing quality (i.e., including more closely spaced orbital exponents and/or a wider range of exponents). These bases may be of "increasing quality" as far as conventional bound-state quantum-chemistry calculations are concerned; however, there is no *a priori* assurance that they are of "increasing quality" for describing metastable states. Also, sequences of electronic configurations lists (e.g., including higher single and double excitations) of "increasing quality" were explored. We wanted to determine: does one get better answers with "better" basis sets and larger configuration lists? And if not, are the answers at least reasonably stable as the basis sets and configuration lists change? Thus our goal was to explore, as basis set quality and configuration lists quality vary, the performance of the OCR and SCR methods.

### 3. Details of the Calculations

#### A. Basis Sets

Our atomic-orbital basis sets were of "graduated quality," as indicated above, with Gaussian functions used exclusively. For  $\text{He}^-$ , all the basis sets (I-IV) were formed using the procedures of Schmidt and Ruedenberg [10] (SR). The four basis sets,  $(8s,4p)$ ,  $(10s,6p)$ ,  $(12s,4p)$ , and  $(14s,5p)$ , were constructed from SRs  $5s,6s,8s$ , and  $10s$  formulas, respectively (SR did not give a  $5s$  basis for He, so basis I was chosen by extrapolation from the parameters they *did* give). In the method of SR, successive exponents  $\zeta_k$  are generated from the even-tempering geometric formula  $\zeta_k = \alpha\beta^k$ , where  $\alpha$  and  $\beta$  are constants and are listed in Tables I and II for He and H. Two additional points about our basis sets should be noted. First, in order to generate more diffuse basis functions,  $k$  was not restricted to be positive (as it is in SR). Second, the He basis sets were all supplemented with a contracted  $(6s/1s)$  He orbital taken from Huzinaga [11]. The more diffuse basis functions are included because it is expected that the  $\text{He}^-$  system should have a more diffuse electron distribution than the He system (for which SR optimized  $\alpha$  and  $\beta$  with  $k > 0$ ). The  $(6s/1s)$  contracted function is included so that all the basis sets treat the ground state of He equally well (which the different SR bases alone do not achieve).

SR did not give  $p$  basis functions for He (or H) since no  $p$  functions are involved in the SCF calculations. In the  $^2S$  resonances under study, the  $p$  orbitals

TABLE I. He basis set parameters.

Basis	Function Type	$\alpha^a$	$\beta^a$	$k_{\min}^b$	$k_{\max}^b$
I	S	.066548	3.9750	-2	+4
	P	.055122	3.1748	+1	+4
II	S	.064848	3.5851	-3	+5
	P	.031250	2.0000	+1	+6
III	S	.061317	3.0693	-4	+6
	P	.055122	3.1748	+1	+4
IV	S	.057797	2.7551	-5	+7
	P	.055108	3.1750	0	+4

<sup>a</sup> All basis sets were supplemented with a (6s/1s) contracted basis function (see text).

<sup>b</sup> Exponents ( $\xi$ ) generated from formula,  $\xi = \alpha\beta^k$  where  $k$  is an integer.

<sup>c</sup>  $k_{\min}$  is the smallest integer  $k$  used in the formula in footnote b;  $k_{\max}$  is the largest value.

are only involved in correlation effects, hence the radial sizes of the  $p$  orbitals should be comparable to those of the  $s$  orbitals used. Thus, we constructed our  $p$  bases by choosing orbital exponents by the method of SR. These exponents cover the same range for all the He basis sets, and give  $p$  orbitals of about the same radial extent as the low-lying  $s$  orbitals.

All four He basis sets described in Table I give reasonably good ground-state and first-excitation energies for neutral He within a full-CI treatment, as shown in Table III. The basis sets can be ranked as IV best, II and III not quite as good, and I poorest. Note, however, that this ranking is based only on performance on neutral He; it says nothing about how well the bases will do for He<sup>-</sup> which is, of course, part of what we want to explore.

A different approach was used to construct the hydrogen atom basis sets. Basis *A* (7s,2p) is Dunning's [12] (4s/3s) basis for hydrogen with four diffuse Gaussians added (following the method of SR). Basis *B* (10s,3p) is a Huzinaga [11] (6s/1s) hydrogen orbital supplemented with Huzinaga's 2s and 4s hydrogen basis functions (partially uncontracted, with the exponents scaled by a factor of 0.75), plus several diffuse  $s$  functions (SR method). In basis *C* (12s,4p), the (6s/1s) function is supplemented with SRs 8s hydrogen basis (using  $k = -4$  to +6). In basis *D* (14s,4p), SRs 10s basis ( $k = -3$  to +10) is used without a (6s/1s) supplement. The  $p$ -orbital exponents used for bases *A-D* approximately span the space covered by Huzinaga's Gaussian contractions for the hydrogen atom 2p Slater orbital.

TABLE II. Hydrogen basis set parameters.

Basis	Function type	$\alpha^a$	$\beta^a$	$k_{\min}^b$	$k_{\max}^b$	
A	s <sup>c</sup>	13.3615	.130844			
		2.0133	.921539			
		.4538	1.00			
		.1233	1.00			
		.0400	1.00			
		.0130	1.00			
		.0034	1.00			
		.0010	1.00			
	p <sup>c</sup>	.600	1.00			
		.150	1.00			
	B	s <sup>c,d</sup>	4.69350	.00843		
			.58274	.05708		
			.48000	1.00		
			.23500	1.00		
.11000			1.00			
.04273			1.00			
.01650			1.00			
.00700			1.00			
.00300			1.00			
.00100			1.00			
p <sup>c</sup>			.25624	.06550		
			.08282	.27049		
		.03120	.52969			
		1.07919	1.00			
		.01250	1.00			
C		s <sup>d</sup>	.030432	2.8437	-4	+6
	p <sup>c</sup>	.020185	.41444			
		.055713	.53150			
		.174211	.18295			
		.733825	.02639			
		1.50000	1.00			
		.01000	1.00			
		.00333	1.00			
D	s	.028905	2.58878	-3	+10	
	p <sup>e</sup>					

<sup>a</sup> See footnote b in Table I.

<sup>b</sup> See footnote c in Table I.

<sup>c</sup> Exponents ( $\xi$ ) are not of the form  $\xi = \alpha\beta^k$  and are listed explicitly. Column 3 lists the exponents and column 4 lists the contraction coefficients, e.g., the first s function in basis A is  $0.130844 \exp(-13.3615 r^2) + 0.921539 \exp(-2.0133 r^2)$ , unnormalized.

<sup>d</sup> A (6s/1s) basis function is also included, see Sec. 3A.

<sup>e</sup> Same p basis as in basis C.

The variation in the hydrogen basis sets is less systematic than in the He basis sets. Basis A is a "standard quantum-chemistry" basis with some allowance made for the more diffuse nature of H<sup>-</sup>. It is included mainly to see whether a poor basis gives poor results. Bases C and D are of similar quality, but of course

TABLE III. Calculated energies for He atom in basis sets I-IV.

Basis	SCF energy	Full CI energy	Full CI 1st excitation energy <sup>a</sup>	subtraction CI 1st excitation energy <sup>b</sup>	
I	-2.764291 au	-2.899518 au	165,580 cm <sup>-1</sup>	162,030 cm <sup>-1</sup> 162,730 162,740	CI list (i) <sup>c</sup> CI list (ii) CI list(iii)
II	-2.861150	-2.899754	165,780	160,310 160,852	CI list (i) CI list (ii)
III	-2.861151	-2.899793	165,700	161,320	
IV	-2.861208	-2.899873	165,530	160,237	
"exact"		-2.904 (Pekeris <sup>16</sup> )	166,530 (experiment <sup>17</sup> )		

<sup>a</sup> This column is the energy difference of the first two eigenvalues of the full-CI secular problem.

<sup>b</sup> Energy difference of the first two roots of the two-electron secular problem used in the SCR method, i.e.,  $E_{n-1}$  ( $N=2$ ). (See the second paragraph of Sec. 2D.)

<sup>c</sup> As noted in the text, several CI lists were used for some of the basis sets.

have no actual exponents in common; should they give very different results, that would indicate that these CR methods are susceptible to "basis set artifact" behavior. Basis set *B*'s relative quality is uncertain; this basis was constructed during early investigations into what constitutes a "good" basis. Table II summarizes these basis sets, and Table IV gives the neutral H atom SCF and full-CI energies for these four basis sets.

### B. Orthonormal Orbitals and Configuration Lists in the CI Calculations

For the hydrogen ion resonance, all calculations were done at the full-CI level, hence the choice of the orthonormal *molecular* orbitals is arbitrary. For

TABLE IV. Calculated energies for H atom basis sets A-D Full CI Excitation Energies<sup>a</sup>

Basis	$E_{\text{SCF}}$	2nd root	3rd root	4th root
A	-4.99339 au	-.124814 au	-.054566 au	-.028381 au
B	-4.99943	-.124981	-.055543	-.031124
C	-4.99943	-.124974	-.055360	-.030550
D	-4.99996	-.124994	-.055483	-.030916
exact	-.500000	-.125000	-.055556	-.031250

<sup>a</sup> Energies for the first (SCF), second, third, and fourth eigenvalues of the full-CI secular problem in the various basis sets.

$\text{He}^-$ , to obtain a reasonable set of molecular orbitals we performed a six-configuration MCSCF ( $1s^2, 1s2s, 2s^2, 2p_x^2, 2p_y^2, 2p_z^2$ ) calculation on neutral He, optimizing the energy for the first excited state. The rationale for this step is that the metastable Feshbach state of  $^2S \text{He}^-$  is approximately described as a  $1s2s$  He atom plus the "incoming electron" occupying another (fairly diffuse)  $s$  orbital. Hence, if our orbitals are appropriate to a  $1s2s$  He first-excited state, then the higher  $s$  orbitals can be used to describe the third electron. The other four configurations in the MCSCF wave function were included to give the most important correlation effects, as well as to improve the lowest  $p$  orbital of each symmetry (which otherwise would have been a Hartree-Fock virtual orbital).

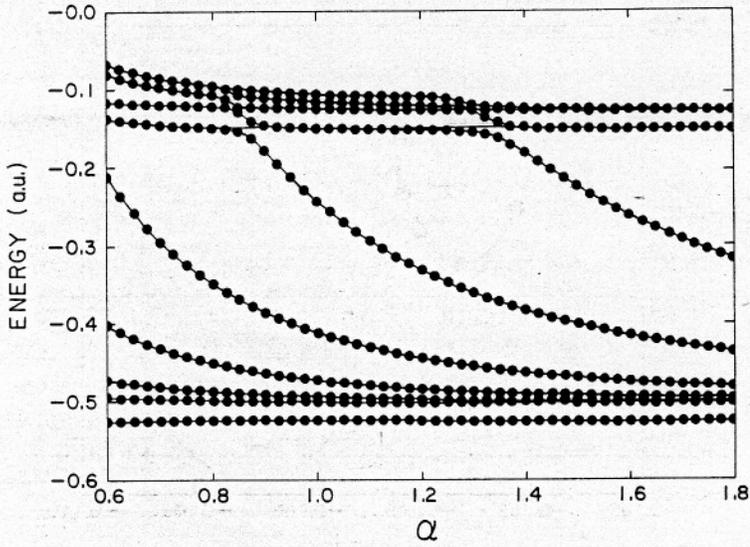
As mentioned above, full-CI calculations were done for hydrogen (H and  $\text{H}^-$ ), thereby "decoupling" the CI effect from the basis set effect. For He and  $\text{He}^-$ , our general philosophy was to allow single and double excitations from the  $1s^2$  core into a small subset of orbitals (including some  $p$  orbitals), and only single excitations into higher  $s$  orbitals. The low-lying single and double excitations relax and correlate the target atom electrons to the incoming electron. Linear combinations of the higher single excitations can simulate the oscillatory behavior of a continuum electron.

### C. Resonance Search Procedure

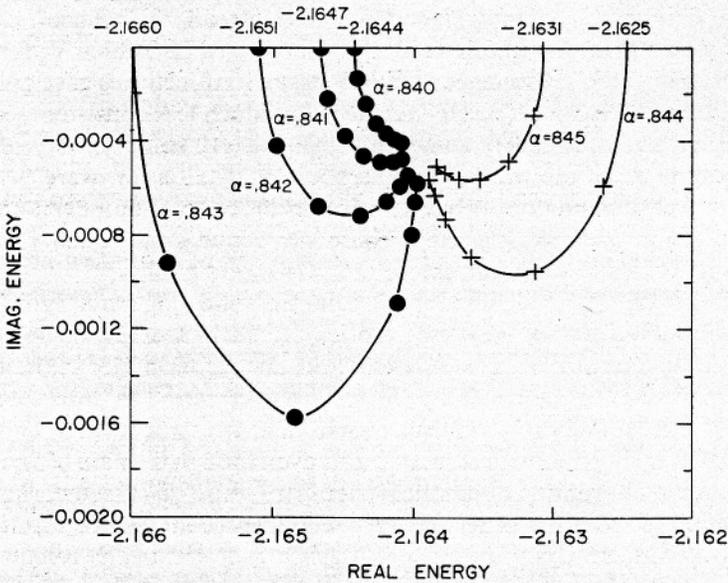
Briefly, the resonance search method used in our calculation can be described as follows. First, we calculate the kinetic energy, the nuclear attraction, and the electron repulsion contributions to the unscaled CI ( $N+1$ )- and  $N$ -electron Hamiltonian matrices. Then, for every desired value of  $\eta$ , these three contributions are scaled by  $\eta^{-2}$ ,  $\eta^{-1}$ , and  $\eta^{-1}$ , respectively, and summed. The resulting scaled CI Hamiltonian matrices are diagonalized by the EISPAC [13] routines for complex general matrices (modified for DEC-20 double precision complex arithmetic by Dr. N. H. F. Beebe). Another value of  $\eta$  is chosen, and the process is repeated. Since  $\eta$  contains two parameters,  $\alpha$  and  $\theta$  one might search extensively before finding the proper  $\alpha$  and the critical value of  $\theta$  [typically, critical  $\theta$  behavior is only observed for a narrow range of  $\alpha$ , since varying  $\alpha$  makes the whole basis more or less diffuse until the basis is optimal for the problem—see Eq. (5)]. A procedure that we have found to work quite well is to set  $\theta$  to zero and vary  $\alpha$  (this corresponds to doing what Taylor and co-workers have called a stabilization calculation [14]). At values of  $\alpha$  which give rise to avoided crossings in graphs of the CI energies versus  $\alpha$  [see Fig. 2(a)], we then vary  $\theta$  and look for "critical- $\theta$ " behavior (this is sometimes referred to in the literature as "computing  $\theta$  trajectories"). Once a reasonable step size for  $\theta$  variation has been determined, we compute several  $\theta$  trajectories for closely spaced values of  $\alpha$ . An especially favorable case is shown in Figure 2(b); a less favorable (perhaps more typical) case is shown in Figure 2(c).

## 4. Results

As noted in Sec. 3B, more than one configuration list was frequently used for a given basis set; furthermore, two resonance search techniques (OCR and



(a)



(b)

Figure 2. (a) Stabilization graph for  $H^-$  resonance. (b)  $He^- \theta$  trajectories. Energies are in a.u. (c)  $H^- \theta$  trajectories. Energies are in a.u.

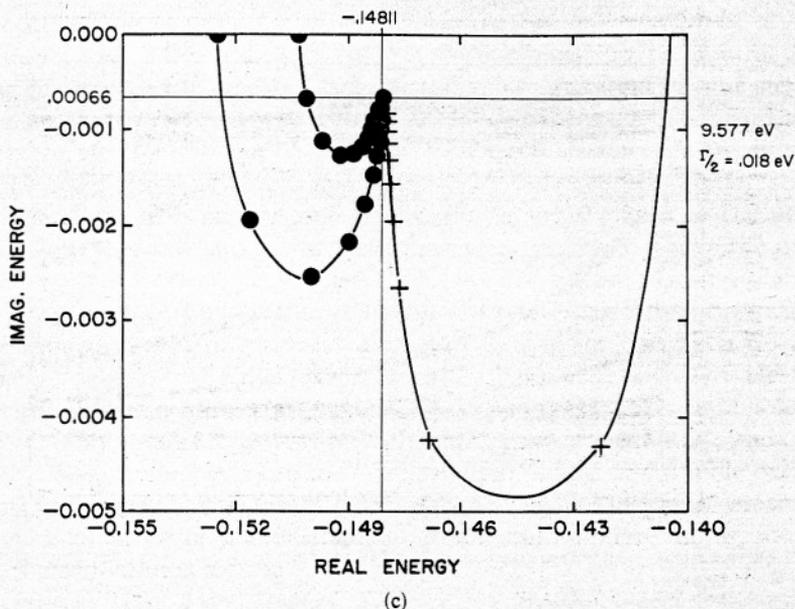


Figure 2. (Continued from the previous page.)

SCR) were employed. As a result, so many  $\theta$  trajectories were generated that it would be impractical to show all such graphs. Instead, the relevant CI energies were extracted from the graphs and are summarized in Tables V (for He) and VI (for H). For the  $H^-$  resonance calculations, all  $\theta$  trajectories gave good critical  $\theta$  behavior (see Sec. 3C). The  $He^-$  results were much less consistent; some were "good" [i.e., as in Fig. 2(b)], some "fair" [Fig. 2(c)], some "poor" (so that no reliable estimate for the width could be obtained), and a few were "very poor" (requiring a certain amount of imagination in order to obtain even an estimate for the position of the resonance). These subjective graph quality ratings are included in Tables V and VI in the columns labeled "quality."

Turning to the  $He^-$  calculations, we note the following from Table V: (i) the generally low "quality" of the  $\theta$ -trajectories; (ii) the lack of any obvious relationship of the OCR results to the SCR results; (iii) the rather major variations in the predicted position of the resonance as the CI list is varied in basis sets I and II; (iv) the SCR results seem to be even worse than the OCR results, and (v) basis sets II and III do not give very similar results even though they are of "comparable quality" in the conventional quantum-chemistry sense discussed earlier.

In summary, both the OCR and SCR techniques seem to give results for  $He^-$  that vary considerably with the details (basis set, CI list) of the calculation. The currently accepted position and width of the  $He^-$  resonance are about 19.4 eV and 10–20 meV, respectively [7]. Our failure to obtain a reasonably stable estimate of the width may be due to its small magnitude (probably zero to the accuracy of the numbers in Table V). Our "best" basis (set IV) does indeed give a position estimate of 19.34 eV. However, owing to the low quality of its  $\theta$

TABLE V. Resonance energies for  $\text{He}^-$ .

Basis/configuration list	Position	Half Width ( $\Gamma/2$ )	Quality
I /i	20.05 eV	NE <sup>a</sup>	poor
	[19.65] <sup>b</sup>	[NE]	[poor]
I/ii	19.75	NE	poor
I/iii	19.73	NE	very poor
II/i	19.29	.013 eV	good
	[19.38]	[NE]	[poor]
II/ii	19.38	.014	fair
	[19.4]	[NE]	[very poor]
III	19.46	.028	good
	[19.51]	[NE]	[poor]
IV	19.34	NE	very poor
	[19.22]	[.003]	[fair]

<sup>a</sup> NE indicates that no reasonable estimate could be made because of the poor quality of  $\theta$  trajectories.

<sup>b</sup> Results enclosed in square brackets refer to those obtained using the SCR method. Others were obtained via the OCR technique.

trajectory, we think it likely that such agreement is merely fortuitous rather than the result of any basis set convergence.

The  $\text{H}^-$  resonance results shown in Table VI illustrate the following: (i) all  $\theta$  trajectories give good critical- $\theta$  behavior, allowing estimates of both the position and width of the resonance; (ii) basis set A (the poorest basis) gives the worst answers; (iii) SCR gives results very comparable to OCR; (iv) in basis sets C and D more than one  $\alpha$ ,  $\theta$  combination gave rise to good critical  $\theta$  behavior, and (v) the two "comparable quality" basis sets (C and D) do indeed give fairly close answers. The "correct answer" is about 9.56 eV for the position and 0.05 eV for the width [3]. Considering the modest extent of these calculations, it seems fair to say that basis set A is the only one that fails to give a reasonable estimate for the complex energy of the resonance.

In addition to the above discussed  $\text{H}^-$  and  $\text{He}^-$  Feshbach resonance calculations, pilot calculations were performed for the  $^2P$  shape resonances in  $\text{Be}^-/\text{Be}$  and  $\text{Mg}^-/\text{Mg}$ . These species are expected to display more substantial core-electron problems than arose in  $\text{H}^-$  and  $\text{He}^-$ . The atomic-orbital basis used for Be was of (5s,7p) quality and two different configuration lists were explored. For Be, only the SCR techniques give any reasonable critical- $\theta$  behavior (the OCR method developed spurious energy variations of the order of 1 Hartree).

TABLE VI. Resonance energies for  $H^-$ .

Basis	Position	Half Width ( $\Gamma/2$ )	Quality	
A	10.17 eV	.0052 eV	good	
	[10.16] <sup>a</sup>	[.0095]	[good]	
B	9.578	.056	good	
	[9.576]	[.056]	[good]	
C	$\alpha = .70$	9.577	.018	good
		[9.577]	[.018]	[good]
	$\alpha = 1.14$	9.584	.033	good
		[9.584]	[.033]	[good]
D	$\alpha = .73$	9.581	.024	good
		[9.578]	[.027]	[good]
	$\alpha = 1.22$	9.588	.033	good
		[9.585]	[.035]	[good]

<sup>a</sup> Results enclosed in square brackets refer to those obtained using the SCR methods. Others were obtained via the OCR technique.

The Be basis used was identical to that employed earlier in Donnelly and Simons' CR Green function study of the  $^2P$  resonance of  $Be^-$  [9]. We used two different configuration lists for Be and obtained two substantially different resonance energy estimates:  $E_r = 0.18$  eV,  $\Gamma/2 = 0.11$  eV and  $E_r = 0.051$  eV,  $\Gamma/2 = 0.014$  eV. Although there is no experimental value and no generally accepted theoretical estimate for the energy of this resonance, the great variations in  $E_r$  and  $\Gamma$  which we observe are discouraging. Interestingly, "good" quality critical- $\theta$  behavior was obtained for both of the CI configuration lists, which leads us to wonder whether the quality of the  $\theta$  trajectories correlates at all with the accuracy of the calculations.

For  $Mg^-/Mg$ , also a  $^2P$  shape resonance, we used the same basis which Donnelly recently used in his successful CR Green's function study [15]. With this basis, we were unable to achieve a reasonable stabilization calculation to obtain an estimate for the optimal  $\alpha$ ; no avoided crossing behavior was noted, and when trial OCR calculations were performed, spurious imaginary contributions to the energy of the order of 20 Hartrees arose. It was clear that we could attach no meaning to the results of such calculations.

The above results illustrate that it is very difficult to choose an atomic-orbital basis set for use in coordinate rotated CI calculations. Frankly, we were rather surprised that even reasonably large standard quantum-chemistry bases (supplemented by diffuse functions) did not yield reliably stable resonance energies.

## 5. Discussion

Based upon our  $H^-/H$  results alone, our conclusions would be quite optimistic. Very cost-effective calculations (which could be made even less expensive by use of an inverse-iteration eigenvalue extraction technique) yielded fairly consistent, good quality results *via* both OCR and SCR, using easily constructed basis sets.

However, the  $He^-$ ,  $Be^-$ , and  $Mg^-$  results are very pessimistic indeed. While the OCR results seem to "bracket" the correct result for  $He^-$ , no systematic basis-set convergence is observed. Furthermore, the cost of the  $He^-$  calculations was *not* so minor; typically a dozen  $\theta$ -trajectories and two or three stabilization calculations (with perhaps 20 points per trajectory) were involved. A complex inverse-iteration routine could not cut down the number of points involved, and might well lead one to miss extracting the proper root of the CI secular problem. For  $Be^-$ , the problem was even worse; about 30  $\theta$  trajectories at various  $\alpha$  values were needed before critical- $\theta$  behavior was even observed. We were totally unsuccessful in finding critical- $\theta$  behavior in the  $Mg^-$  problem. In summary, it appears that OCR and SCR cannot be straightforwardly applied using conventional basis sets and electronic configuration lists. It also appears that SCR does not have any advantages over OCR. If SCR is worse than OCR for a two-electron problem, it is unlikely that it has anything to offer for larger systems. We therefore consider our study of SCR to be an unsuccessful numerical experiment.

The OCR method itself appears to have bleak prospects for successful use on even moderately large systems; the spurious (core) energy variations with  $\eta$  are so large that they obscure any stationary behavior in the  $\theta$  trajectories. Hence we think it wise to look with caution at results, for many-electron targets, of any calculations based on techniques resembling OCR or SCR. The extension of either OCR or SCR to larger systems should be done in conjunction with careful basis set and CI list variation studies.

The results presented here provide, in our opinion, strong motivation to proceed toward developing well-founded and computationally tractable methods which permit one to apply coordinate rotation to only the one *active* electron. As mentioned earlier, other workers have indeed made some progress along these lines. A great deal of formal and computational work remains to be done before it becomes clear which implementation of CR theory is optimal. Clearly, even within the approaches mentioned in Sec. 2C, atomic-orbital basis-set dependence must be carefully considered. However, it is hoped that, by formally removing the inner (core) orbitals from direct consideration in the CR process,

one can avoid the need for large "tight" basis sets whose purpose is to describe these rotated core orbitals.

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