Stabilization Calculations of the Low-Lying Temporary Anions States of Be, Mg, and Ca

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The stabilization method is used in conjunction with the equation-of-motion electron-attachment coupled-cluster method to calculate the complex energies of the 2P temporary anion states of Be and Mg as well as of the 2D temporary anions states of Mg and Ca. The calculated resonance parameters for the 2P state of Mg⁻ and 2D state of Ca⁻ agree well with experiment. Experimental results are not available for the 2P anion of Be, but we note that our calculated resonance parameters of 2P Be⁻, while in good agreement with the CI results of McNutt and McCurdy (1983), differ significantly from the results of two other recent theoretical studies.

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I. Introduction

The temporary anion states of Be, Mg, and Ca have been the subject of several experimental[1–4] and theoretical[5–11] studies. The anion states of these atoms have been reviewed relatively recently.[12,13] The ground state $(ns^2np)^2P$ anions of Be and Mg are unbound and, thus, correspond to shape resonances. While the $(4s^24p)^2P$ anion state of Ca is weakly bound with a detachment energy of about 20 meV,[14–19] electron transmission spectroscopy (ETS)[20] measurements show that Ca displays a relative low-lying $(4s^24d)^2D$ shape resonance.[2] In addition, the electron transmission spectra of Mg and Ca display additional low-lying resonances that have been attributed to 2D and $^2S (nsnp^2)$ core-excited anion states.[1–4]

The 2P resonance of Be has been the subject of numerous theoretical studies, which give a surprisingly large spread in the values of the resonance parameters. Much less theoretical work has been done on the low-lying anion states of Mg and Ca. These considerations have motivated us to undertake stabilization calculations[7,21–24] of the low-lying temporary anion states of Be, Mg, and Ca, using the equation-of-motion electron-attachment coupled-cluster method restricted to single and double excitations (EOM-EA-CCSD).[25] This approach, when used with suitable basis sets, has been found to provide an accurate characterization of the temporary anion states of N_2 , CO, and other molecules.[24,26]

II. Methodology

The EOM-EA-CCSD calculations were carried out correlating all electrons and using the aug-cc-pCVXZ basis sets[27–30] supplemented with large sets of diffuse p and d functions for calculations on 2P and 2D shape resonances, respectively. The "C" indicates that the basis set includes functions appropriate for correlating the core, and $X = D, T$, and Q , denote double, triple, and quadrupole zeta quality basis sets, respectively. For Be supplemented aug-cc-pCVDZ, aug-cc-pCVTZ, and aug-cc-pCVQZ basis sets were employed to monitor the convergence of the resonance parameters with increasing basis set flexibility, while for Mg and Ca, only the supplemented aug-cc-pCVQZ basis set was employed. For the 2P anion states the aug p functions of the aug-cc-pCVXZ basis sets were replaced by a set of nine even-tempered p

functions which were scaled in the stabilization calculations. The largest exponent of these diffuse sets were 0.02 and 0.01 for Be and Mg, respectively. In both cases each successive exponent was half of the previous one. For the 2D state of Mg^- the two most diffuse p functions in the aug-cc-pCVQZ basis set were replaced with an even tempered set of five p functions with the largest exponent being 0.15 and each successive exponent being half of the previous one together with an additional d function with exponent 0.02. In the stabilization calculations on this state the five diffuse p and the two diffuse d functions were scaled. In the case of the 2D state of Ca^- the cc-p-CVQZ basis set was augmented with diffuse s , p , f , and g functions with exponents 0.008318, 0.008, 0.04, and 0.05, respectively. In addition, three diffuse d functions with exponents of 0.015, 0.0075, and 0.00375 were added. The diffuse p and diffuse d functions were scaled in the stabilization calculations. Stabilization calculations were also carried out using the full configuration interaction (CI) method on the anion state of Be, allowing us to establish the appropriateness of the EOM-EA-CCSD method.

In order to generate the stabilization graphs, the exponents of the supplemental diffuse functions were scaled by a factor, α , and the calculations were carried out for α values ranging from 0.35 to 2.0. These results were then analytically continued into the complex energy plane using the approach of Chao *et al.*[7] The resulting expression was differentiated to find the stationary points (i.e., the value of α , denoted α^* , for which $\partial E / \partial \alpha = 0$). The complex resonance energy is then given by $E(\alpha^*) = E_R - i\Gamma/2$ where E_R is the resonance position, and Γ its width.[31,32] Although several functional forms for $E(\alpha)$ have been employed in the literature, it is now generally recognized that, since stabilization graphs involve avoided crossings between diabatic states corresponding to the anion and discretized continuum solutions, it is important to adopt a functional form that incorporates the branch singularities. This can be accomplished by use of generalized Padé approximants (GPA).[33,34] The simplest GPA that incorporates the branch structure associated with a two-root avoided crossing is:

$$P(\alpha) E^2 + Q(\alpha) E + R(\alpha) = 0 \quad (1)$$

where P , Q , and R are polynomials in α whose coefficients are determined by fitting to the calculated energies for real values of α . Equation 1 is appropriate for stabilization graphs with well separated avoided crossings. If there are two or more close avoided crossings, the GPA can be generalized by including higher order terms in E with associated polynomials in α .

In the present study we include up to five roots in the analytic continuation process, always including the three most clearly interacting roots, and we employed polynomials of order 10 – 14. Similar values of the resonance parameters were obtained when using the three to five root extensions of Eq. 1, when employing the different order polynomials, and when using different choices of the input data points. The reported resonance parameters are obtained by averaging over the results obtained from the different calculations.

The EOM-EA-CCSD calculations were carried out using the CFOUR code,[35] and the full CI calculations were carried out using the PSI4 code.[36,37]

III. Results

Figures 1-4 display the stabilization graphs of the 2P states of Be and Mg and of the 2D states of Mg and Ca plus an excess electron. In each case, we have also included the energies of the discretized continuum (DC) functions,[7,38] obtained from calculations using the same basis set as used in the stabilization calculations but in the absence of the nuclei and electrons of the atoms. Typically, stabilization graphs display well-defined avoided crossings, which in a diabatic picture can be viewed as arising from the interaction between a discrete state and discretized continuum states. Although the avoided crossings in the 2P stabilization graphs of Be and Mg are not very pronounced, it is clear that the EOM-EA-CCSD calculations give one more root near 0.3 eV than there are DC solutions, indicating the presence of resonance states. In the EOM-EA-CCSD calculations the solutions corresponding to DC states must be orthogonal to lower energy states of the same symmetry, which causes DC solutions above the resonance in energy to be destabilized relative to the energies determined with the nuclei and electrons

removed. Table I summarizes the resonance parameters obtained in the present study using the EOM-EA-CCSD calculations together with the supplemented aug-cc-pCVQZ basis sets as well as results from experiment and prior ab initio theoretical studies including the effects of electron correlation. We now discuss the results for each atom individually.

Figure 1. Stabilization graph for the 2P state of Be^- calculated using the EOM-EA-CCSD method and the supplemented aug-cc-pCVQZ basis. The EOM-EA-CCSD energies are given by blue dots, and the energies of the DC solutions are indicated by the dashed black lines.

Figure 2. Stabilization graph for the 2P state of Mg^+ calculated using the EOM-EA-CCSD method and the supplemented aug-cc-pCVQZ basis set. The EOM-EA-CCSD energies are reported as blue dots, and the energies of the DC solutions are shown as dashed black lines.

Figure 3. Stabilization graph for 2D states of Mg^+ calculated using the EOM-EA-CCSD method and the supplemented aug-cc-pCVQZ basis set. The EOM-EA-CCSD energies are shown as blue dots, and the energies of the DC solutions as dashed black lines.

Figure 4. Stabilization graph for the 2D state of Ca obtained using the EOM-EA-CCSD method supplemented aug-cc-pCVQZ basis. The EOM-EA-CCSD energies are indicated as blue dots and the energies of the DC solutions as dashed black lines.

A. Be:

Our EOM-EA-CCSD calculations on the $(2s^22p)^2P$ anion of Be using basis sets ranging from aug-cc-pCVDZ to aug-cc-pCVQZ all give essentially the same resonance parameters, as determined using the stabilization method. With the largest basis set considered, the resonance parameters are $E_R = 0.33$ and $\Gamma = 0.40$ eV. Full CI calculations were carried out for the two smaller basis sets and found gives resonance parameters within 0.02 eV of the EOM-CCSD results. Our resonance parameters for Be are in

excellent agreement with the results of McNutt and McCurdy,[8] who, for the anion, carried out a single, double, triple excitation CI calculation using complex SCF orbitals (CSCF/SDTCI). They are also in good agreement with the results of complex scaling multiconfigurational self-consistent field CMSCF($2s2p3s3p3d$) calculations of Samanta and Yeager, where the orbitals active in the MCSCF space are indicated in parentheses.[10] (Samanta and Yeager actually reported two 2P resonances for Be^- , one with $E_R = 0.31$ and $\Gamma = 0.49$ eV and the other with $E_R = 0.73$ and $\Gamma = 1.58$ eV. In the above comparison we have used the first set of results.) On the other hand, our resonance parameters of $^2P \text{ Be}^-$ differ significantly from those from recent complex absorbing potential (CAP)[39] calculations of Jagau *et al.*[6] and from the recent complex scaled multiconfigurational spin-tensor electron propagator (CMCSTEP) calculations of Tsednee and Yeager.[9] These two calculations place the 2P resonance much higher in energy (~ 0.8 eV) than our calculations and those of McNutt and McCurdy[8] both of which place it near 0.3 eV. We note also that the CAP and CMCSTEP calculations give very different widths (0.12 vs. 0.79 eV) for $^2P \text{ Be}^-$. The value of the width from the CAP calculations seems much too small in light of the fact that for all other theoretical results summarized in Table 1 the width of the resonance is comparable to its real part. This leads us to question whether the CAP potential is significantly perturbing the anion state. In the case of the CMCSTEP calculations, it is possible that a larger active orbital space is required to obtain well-converged results for Be^- . Stabilization calculations using the EOM-EA-CCSD method and the basis set of Jagau *et al.*[6] (which was also tested by Tsednee and Yeager[9]) provide resonance parameters close to those reported here, eliminating basis set differences as a source of the discrepancy. As noted above, there are no experimental results on the temporary anion states of Be.

B. Mg

The EOM-EA-CCSD calculations give resonance parameters of $E_R = 0.22$ and $\Gamma = 0.24$ eV for the $(3s^23p) ^2P$ anion of Mg. These are in reasonable agreement with the $E_R = 0.15$ and $\Gamma = 0.14$ eV values deduced from ETS measurements.[3,4] However, we note that the experimental value of the width was

associated with the energy difference between the dip and peak in the ET spectrum measured in the derivative mode, while for a resonance with an ideal Breit-Wigner line shape the energy difference between the dip and peak associated with the resonance in the ET spectrum actually corresponds to $\Gamma/\sqrt{3}$, [2] which would give a value of $\Gamma = 0.24$ eV, identical to that from the EOM calculations. The real part of the resonance energy calculated here is in good agreement with the result of the CMCSTEP calculations of Tsednee and Yeager[9], whereas the width is approximately a factor of two larger.

Figure 3 displays the stabilization graph for 2D states of Mg^- calculated using the EOM-EA-CCSD method with the supplemented aug-cc-pCVQZ basis set. The stabilization graph near 3 eV is somewhat unusual. In addition to a strong avoided crossing between the second and fourth roots near $\alpha = 0.9$, there is a curve of nearly constant energy (corresponding to the third root) present in the crossing region. The constant energy feature in the stabilization graph arises from the $3s^1 3p^1$ excited state of neutral Mg (experimentally located at 2.71 eV) plus a free electron in a diffuse p symmetry DC orbital. We find that electronically excited states of the neutral species frequently appear in stabilization graphs that extend to energies above the excitation energy. Application of the stabilization method to the data points in the avoided crossing region gives resonance parameters of $E_R = 3.3$ eV, $\Gamma = 0.12$ eV. The ETS spectrum of Mg has feature at 2.9 eV with a width of 0.14 eV (deduced assuming a Breit-Wigner line shape) which has been interpreted as arising from a $3s^1 3p^2$ (2D) core-excited resonance. Examination of the CI vector of the second root near $\alpha = 1$, reveals that the resonance is dominated by $3s^1 3p^2$ configurations, consistent with the assignment of Ref. 3.

C. Ca

At the level of theory employed here, the $(4s^2 4p) ^2P$ anion state of Ca is predicted to be slightly unbound, while it has been established in earlier studies that this anion state is weakly bound.[15,16] The 2P anion state of Ca is known to be an especially challenging system for theory, requiring, among other things, the inclusion of relativistic effects.[16] Our EOM-EA-CCSD calculations give $E_R = 1.32$ eV and $\Gamma = 0.97$ eV for the $(4s^2 3d) ^2D$ anion, as compared with the $E_R = 1.1 \pm 0.15$ eV and $\Gamma = 0.5 \pm 0.1$ eV

values derived from electron transmission measurements. As for Mg, the reported value of the width from the ETS measurements simply associated the width with the dip to peak energy difference. If one applies the $\sqrt{3}$ factor discussed above, one obtains a value of 0.9 eV for the experimental width, in good agreement with our calculated result. Our resonance parameters for the 2D state of Ca^- are also in reasonable agreement of those from the CMCSTEP calculations.[9] Examination of the CI vector in the vicinity of the avoided crossing in the stabilization graph reveals that this resonance has about ten percent $4s4p^2$ character. The greater width of the resonance in Ca compared to the 2D state of Mg is likely due to the greater single particle character in the 2D state of Ca.

IV. Conclusions

The EOM-EA-CCSD method has been used with large basis sets and the stabilization method to characterize the low energy temporary anion states of Be, Mg, and Ca. For the 2P states of Be and Mg anions and for the 2D state of the Ca^- the width of the anion state is roughly comparable to its position. It should be noted that for "ideal" resonances which are well fit by the Breit-Wigner expression, the resonance width should be much smaller than the resonance position. In such cases, it is difficult to extract a well-defined width from the experiments, and judging the performance of theory would best be done by comparison of the calculated and measured cross sections. Methods that are designed to locate the pole in the S-matrix associated with the resonance (including the stabilization method used here), do not give the cross sections unless combined with an assumed expression for the line shape.

The use of the EOM-EA-CCSD method with the exponent scaling version of the stabilization method has not been used before to characterize temporary anion states dominated by core-excited character. While the approach proved to be reasonably successful for the 2D state of Mg^- , in general, one would expect that such states would require inclusion of higher level excitations in the EOM calculations.

In the case of the 2P state of Be^- different theoretical approaches give very different values of the resonance parameters. The system warrants further theoretical study.

Table I. Resonance parameters (eV) for Be, Mg, Ca

Method	E_R	Γ
Be (2P)		
CAP[6/6/6] ^a	0.79	0.12
CSCF/SDTCI ^b	0.32	0.30
CMSCF ^c	0.31	0.40
CMCSTEP(2s2p3s3p3d) ^d	0.76	0.79
Present study	0.33	0.40
Mg(2P)		
CMCSTEP(3s3p4s4p3d) ^d	0.20	0.13
Present study	0.22	0.24
Experiment ^e	0.15 ± 0.03	$0.14 (0.24)^g$
Mg(2D)		
CMCSTEP(3s3p4s4p3d) ^d	4.04	2.00
Present study	3.3	0.12
Experiment ^e	2.8 ± 0.15	$0.08 (0.14)^g$
Ca(2D)		
CMCSTEP(4s4p5s5p3d) ^d	1.16	0.62
Present study	1.32	0.97
Experiment ^f	1.1 ± 0.15	$0.5 \pm 0.1 (0.9)$

^aRef. 6, ^bRef. 8, ^cRef 10, ^dRef. 9, ^eRef. 3, ^fRef. 2, ^gNumbers in parenthesis indicate the width obtained using the adjustment by a factor of $\sqrt{3}$, as discussed in the text.

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