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Calculation of ^2P shape resonances in Be and Mg

Henry A. Kurtz* and Yngve Öhrn

Quantum Theory Project, Department of Chemistry, University of Florida, Gainesville, Florida 32611

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Shape resonances of ^2P type are calculated for electron scattering with Be and Mg target atoms using the Harris method with an *ad hoc* polarization potential. Good agreements are obtained for resonance energies and widths.

I. INTRODUCTION

In recent years, considerable progress has been made in the calculation of resonances in electron scattering with both atomic and molecular targets. Several good reviews on resonances (also known as temporary negative ions or compound states) have been given.[1] Electron scattering resonances can be separated into three classifications[1(b)]: core excited type I (also called Feshbach resonances), core excited type II (excited state shape resonances), and single-particle resonances. The particular type of resonances which will be of concern here is the single-particle resonances. They are also shape resonances since the angular momentum of the electron forms a penetrable barrier in the potential via the centrifugal term $l(l+1)/2r^2$, which serves to trap the electron. Such resonances are expected to be seen only in p and higher partial waves. For single-particle resonances there are no target excitations, as in core excited type II, and they can be used as the definition of *negative* electron affinities.

Single-particle resonances have been observed for the group-II elements Mg, Zn, Cd, and Hg by Burrow *et al.*[2] These systems are ideal for observing shape resonances because they provide a low-lying unoccupied np orbital for the incoming electron, resulting in a ^2P resonance. Unfortunately, measurements of the Be resonance have not been made due to the high toxicity of the substance.

The anion states of Be and Mg are of considerable interest. For both Be and Mg, there is possibly a ^2S state due to an electron occupying a $3s$ and $4s$ orbital, respectively. Such states are predicted by isoelectronic extrapolation techniques[3] to lie below the corresponding ^2P states. These states do not exhibit a centrifugal barrier to trap the incoming electron and, therefore, will not appear as shape resonances in the elastic cross sections. The ^2S state of Be$^-$ is predicted to be bound by extrapolation procedures but this has not been substantiated by *ab initio* calculations.[4] We refer the reader to the work of Massey[5] for a more detailed discussion of these states.

Relatively few calculations on the ^2P resonances have been done for Be and Mg. Hunt and Moiseiwitsch[6] carried out elastic scattering calculations on a variety of atoms using a model potential and recently Rescigno *et al.*[7] have performed static-exchange calculations on Be using the complex coordinate method.

Other cases in which one might expect to find shape resonances are the rare-gas atoms, but for these systems the incoming electron would have to occupy an orbital of the next higher n quantum number. Hence, the additional electron will be at a large radial distance and see little of the potential required to localize it. Another important difference is in the polarizabilities of these atoms, which are much smaller than those of the group-II atoms. Because of these factors, shape resonances for rare-gas atoms will probably not be discernable from the background elastic scattering cross section.

II. METHOD OF CALCULATION

When a partial-wave expansion of the scattering function is made, the resulting equations to be solved are

$$\left(-\frac{1}{2}\frac{d^2}{dr^2}+\frac{l(l+1)}{2r^2}+V(r)\right)\Psi_l=E\Psi_l\,. \tag{1}$$

The momentum of the scattered electron, k, is given by $k=(2E)^{1/2}$.

We use the Harris method[8] to solve the above equations. In this method the scattering wave function is represented as

$$\Psi_l=s_l+tc_l+\sum_i b_i u_i\,, \tag{2}$$

where s_l and c_l are functions that go asymptotically (where V goes to zero) as j_l and n_l, the spherical Bessel and Neuman functions, respectively. From this expression, t can be identified as $\tan\delta_l$, the tangent of the phase shift. The functions u_i are a set of L^2 functions which describe the wave packet near the atom and go to zero asymptotically.

If the target is chosen to be represented by the Hartree-Fock approximation (static exchange), we write

$$V(r) = V_{\rm HF} , \tag{3}$$

and the u_i's are the virtual Hartree-Fock orbitals.

In order to evaluate the integrals to obtain the phase shift δ_l, we must choose an explicit form for s_l and c_l. The following choice of Harris and Michels[9] is used in our calculations:

$$\begin{aligned} s_l &= j_l(kr) , \\ c_l &= j_{l+1}(kr) + \frac{l(l+1)}{kr} j_{l+2}(kr) \underset{r\to\infty}{\simeq} n_l , \end{aligned} \tag{4}$$

where the latter approximation to n_l is due to Armstead.[10]

Many authors have studied the evaluation of the two-electron integrals with a scattering function[9,11] which are needed for the remaining terms. One additional integral must be evaluated when using the approximate form of n_l for c_l. This is $\langle u_i | T_l - \frac{1}{2}k^2 | c_l \rangle$, which arises because c_l is not an eigenfunction of the kinetic energy T_l as is j_l. The main advantage of this method is that integrals involving only a single scattering function need to be evaluated and they can be done *analytically*.

The atoms studied here are highly polarizable and, therefore, the static-exchange approximation is expected to be inadequate. We include polarization effects in our calculations with a modified potential of the form

$$V(r) = V_{\rm HF} + V_{\rm pol}(r) , \tag{5}$$

where

$$V_{\rm pol} = \begin{cases} -\alpha/2r^4, & r > r_0 \\ -\alpha r/2r_0^5, & r < r_0 . \end{cases} \tag{6}$$

The parameter α is the static polarizability and r_0 is an arbitrary cutoff parameter. Potentials of this type have been studied by Truhlar *et al.*[12]

In order to use a potential of this form, some method must be chosen to obtain a value of r_0. In this work we have arbitrarily chosen r_0 as the distance at which the centrifugal barrier plus polarization is zero. The choice is meaningful only for $l \neq 0$, as is the case for the systems in question, and gives rise to the expression

$$r_0 = [\alpha / l(l+1)]^{1/2} .$$

If a polarization potential is included, the functions u_i in Eq. (2) must now be eigenfunctions of $L = F + V_{\rm pol}$ instead of the Fock operator F. Also the additional integrals $\langle u_i | V_{\rm pol} | s_l \rangle$ and $\langle u_i | V_{\rm pol} | c_l \rangle$ must be calculated.

A shortcoming of the Harris method is that the scattering quantities can only be evaluated at discrete energy values. Since these values are obtained as positive eigenvalues of a particular Hamiltonian, it is not possible *a priori* to select a given scattering energy. The systems studied here are of relatively small size, and therefore several large basis sets can be employed to generate many energy values. If the quantities in question do not undergo rapid variations between the available energies, this method does not present any difficulties in determining the overall energy dependence by some means of interpolation.

III. CALCULATION OF δ_l AND δ_l

To describe the target beryllium atom, Clementi's[13] extended STO Hartree-Fock solutions were used for the 1*s* and 2*s* orbitals. This basis gives a total self-consistent field (SCF) energy of −14.573 02 a.u. These functions were augmented with 12 p_0 orbitals to provide the needed *p* virtual orbitals and energies. Three different sets of functions were used to provide a distribution of energies over the range of interest and these are shown in Table I. The *p*-wave phase shifts and partial cross sections were then calculated in the static-exchange approximation. In order to calculate the phase shifts and partial cross sections in the static-exchange plus polarization approximation, the static polarizability α of Be used was 47 a.u. with the cutoff parameter r_0 chosen as 5 bohrs. The results of the two calculations are summarized in Table II for energies less than 7.5 eV. A plot of the phase shifts and partial cross sections are given in Figs. 1 and 2, respectively. From these graphs it is easy to see that polarization effects are very important in describing the resonance in Be.

The process used for Mg is similar to that used

TABLE I. Additional Be p_0 functions.

Set I	Set II	Set III
1.900	2.000	2.100
1.400	1.500	1.600
0.900	1.000	1.100
0.700	0.750	0.800
0.450	0.500	0.550
0.350	0.375	0.400
0.220	0.250	0.280
0.170	0.180	0.190
0.110	0.120	0.130
0.085	0.090	0.095
0.055	0.060	0.065
0.025	0.030	0.035

TABLE II. Be results.

Static exchange Energy (eV)	δ_1 (rad)	σ_1 (a.u.^{2})	Static exchange + polarization Energy (eV)	δ_1 (rad)	σ_1 (a.u.^{2})
0.0042	0.0001	0.0024	0.0042	0.0030	1.1325
0.0055	0.0002	0.0040	0.0054	0.0040	1.5237
0.0068	0.0003	0.0064	0.0068	0.0051	1.9967
0.0184	0.0016	0.0693	0.0182	0.0197	10.8887
0.0226	0.0022	0.1050	0.0224	0.0258	15.2638
0.0272	0.0028	0.1521	0.0268	0.0328	20.6289
0.0542	0.0080	0.6089	0.0527	0.0837	67.9889
0.0650	0.0107	0.9071	0.0628	0.1085	95.7466
0.0767	0.0139	1.3019	0.0734	0.1383	132.7036
0.1338	0.0352	4.7537	0.1215	0.3356	457.8664
0.1586	0.0461	6.8721	0.1401	0.4359	652.4380
0.1854	0.0591	9.6559	0.1586	0.5492	880.9481
0.3000	0.1285	28.0907	0.2313	1.0497	1667.7666
0.3524	0.1692	41.2480	0.2618	1.2441	1757.3047
0.4070	0.2167	58.2635	0.2940	1.4150	1702.4255
0.6087	0.4409	153.4354	0.4311	1.8184	1118.4447
0.7012	0.5541	202.4999	0.5030	1.8979	914.3762
0.7953	0.6709	249.2473	0.5828	1.9452	762.3221
1.1433	1.0298	329.6384	0.9212	1.9645	474.8625
1.3166	1.1574	326.7206	1.0987	1.9511	402.5179
1.5053	1.2577	308.3944	1.2930	1.9308	347.4711
2.2525	1.4430	224.0107	2.0505	1.8601	229.7704
2.6585	1.4692	190.9507	2.4545	1.8214	196.1158
3.1057	1.4779	163.7279	2.8958	1.7846	169.1473
5.0173	1.4225	99.9954	4.7316	1.6661	107.4190
5.9656	1.4019	83.5482	5.6393	1.6297	90.6379
6.9973	1.3809	70.6895	6.6252	1.6002	77.3511

for Be. Clementi's[13] extended STO Hartree-Fock solutions were used to describe the target $1s$, $2s$, $2p$, and $3s$ orbitals which give a total SCF energy of −199.614 58 a.u. These were then augmented with three sets of p_0 functions to produce virtual orbitals. Unlike the Be sets, these functions consisted of only two different exponents with n quantum numbers running from 3 to 7 for each. All three sets consisted of functions with one exponent equal to unity and the remaining one assuming the values of 0.30, 0.325, and 0.35, respectively. For the calculations which included polarization, the static polarizability used was 81 a.u. with a cutoff

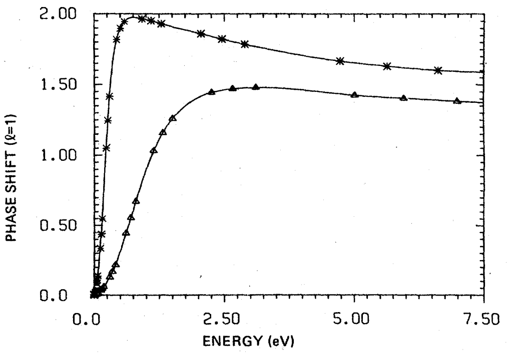

FIG. 1. Be $l=1$ phase-shift curves. The points labeled by Δ were obtained using the static-exchange potential and those labeled by * were obtained using the polarization plus static-exchange potential.

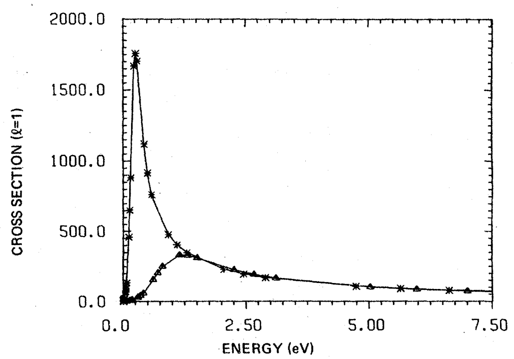

FIG. 2. Be $l=1$ cross-section curves with and without polarization. For an explanation of the labeling see Fig. 1.

of 6.3 bohrs. The results below 7.5 eV are summarized in Table III with plots of δ_l and σ_l shown in Figs. 3 and 4, respectively.

IV. EVALUATION OF RESONANCE PARAMETERS

The resonance energies and widths can be obtained from the phase shift curves via the method of time delay.[14] The time an outgoing particle is delayed due to the presence of a potential is given by

$$\Delta t = 2n \frac{d\delta}{dE}. \tag{7}$$

The energy of maximum time delay is identified as the resonance energy E_r, and the width Γ is given by

$$\frac{2}{\Gamma} = \left.\frac{d\delta}{dE}\right|_{E=E_r}. \tag{8}$$

To actually solve for E_r and Γ from the previously calculated phase shifts, the values of the first and second derivatives of each curve are used. To obtain these, the phase-shift values were fit with a cubic spline and the first and second derivatives then evaluated at the known energies. These quantities were then, in return, fit with cubic splines to provide continuous curves for interpolation. The second derivative curve was used to define the energy E_r because it is more accurate to interpolate the zero of this curve than the maximum of the first derivative. The width Γ is then found by evaluating the first derivative at E_r. Table IV shows the calculated resonance energies and widths for Be and Mg and a comparison with other results.

The accuracy of the resonance positions and widths is dependent on the accuracy of interpolation using the spline fits. We feel that we have enough points in the region of interest so that the cubic spline fits do not introduce any spurious behavior and that our calculated quantities are precise.

V. CONCLUSIONS

As can be seen from Figs. 2 and 4, polarization effects play a very important role in calculating accurate resonance energies and widths for the highly polarizable group-II atoms. The results of this work are highly dependent on the semiempirical polarization potential used and further study of the methods of choosing the parameters is needed. Other methods of including polarization are also worth further study, in particular the *ab initio* (second-order) optical potential.[15] Such potentials would increase the computational effort required for this method, but could be used with a discrete basis and would be interesting to try.

In comparing our resonance positions with the experimental one, it should be noted that the latter were estimated by the maximum in the total cross

TABLE III. Mg results.

Static exchange			Static exchange + polarization		
Energy (eV)	δ_1 (rad)	σ_1 (a.u.^{2})	Energy (eV)	δ_1 (rad)	δ_1 (a.u.^{2})
0.0818	0.0212	2.8035	0.0718	0.1879	249.0809
0.0929	0.0257	3.6478	0.0796	0.2186	302.9130
0.1041	0.0307	4.6316	0.0871	0.2495	359.0384
0.2518	0.1531	47.3775	0.1814	1.0416	2106.5748
0.2825	0.1846	61.1360	0.1984	1.1570	2167.3577
0.3131	0.2179	76.5687	0.2156	1.2597	2154.1128
0.5237	0.5152	237.7273	0.3878	1.7450	1282.9533
0.5797	0.5927	276.0759	0.4360	1.7765	1127.3356
0.6352	0.6665	308.6260	0.4860	1.7949	1003.2621
0.9517	0.9941	378.7139	0.8090	1.7889	604.3531
1.0531	1.0574	369.5619	0.9123	1.7706	540.0515
1.1566	1.1068	354.6390	1.0181	1.7497	487.8392
1.7422	1.2139	258.4543	1.6124	1.6186	317.3692
1.9283	1.2207	234.7038	1.8012	1.5848	284.7117
2.1169	1.2207	213.7889	1.9915	1.5528	257.4616
3.3015	1.1425	128.5517	3.1542	1.3813	156.8413
3.6084	1.1229	115.4799	3.4583	1.3511	141.2673
3.9171	1.1024	104.2571	3.7631	1.3229	128.0946
6.4047	0.9314	51.5651	6.1448	1.1334	68.4913
6.8692	0.9082	46.4105	6.6005	1.1073	62.1744
7.3382	0.8855	41.9011	7.0612	1.0814	56.5881

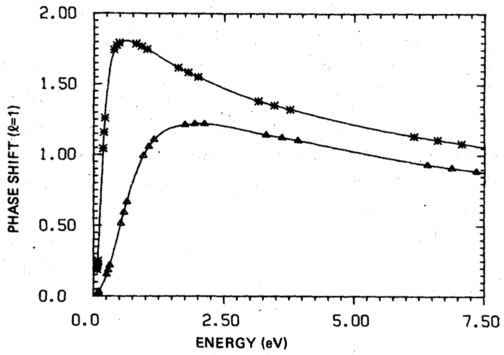

FIG. 3. Mg $l=1$ phase-shift curves with with and without polarization. For an explanation of the labeling, see Fig. 1.

section. From our partial cross sections, this maximum is seen to lie slightly above the calculated resonance position. The position of the maximum in the partial cross section may not correspond exactly to that in the total cross section, which may be shifted slightly due to the large, broad s-wave component not given in our calculations. The experimental widths were determined as the distance between the maximum positive and negative slopes of the total cross section.

The results of Rescigno *et al.*[7] provide a good check on our procedures. They used the same static-exchange potential in their method and, hence, should obtain the same results. Indeed, our static-exchange results are in very good agreement with theirs.

Hunt and Moiseiwitsch[6] have also performed elastic scattering calculations on Be and Mg using a model potential of the form

$$V(c)=\begin{cases}-z(1/r-1/r_0)\,, & r<r_0\\ 0\,, & r>r_0\end{cases} \qquad (9)$$

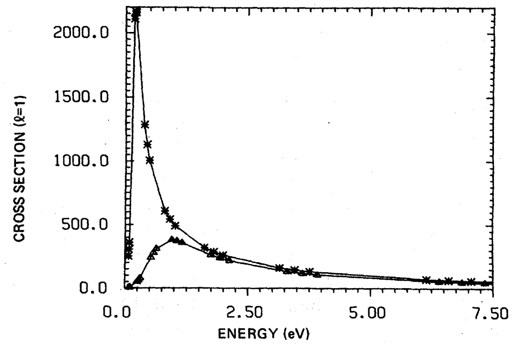

FIG. 4. Mg $l=1$ cross-section curves with and without polarization. For an explanation of the labeling see Fig. 1.

TABLE IV. Resonance parameters.

Beryllium:	E_r	Γ
SE[a]	0.769	1.611
SEP[b]	0.195	0.283
HM[c]	0.60	0.22
RMO[d]	0.76	1.11
Magnesium:	R_r	Γ
SE	0.460	1.374
SEP	0.161	0.238
HM	0.37	0.10
Robb[e]	0.166	···
Expt.	0.15	0.14

[a] Static exchange (this work).

[b] Static exchange + polarization (this work).

[c] Reference 6.

[d] Reference 7.

[e] W. D. Robb (unpublished results from Ref. 2).

[f] Reference 2.

where the parameter r_0 was chosen by an isoelectronic extrapolation procedure. This potential does not allow for the long range $-\alpha/2r^4$ attractive polarization potential, and this is likely the reason for their resonance position to possibly be too high. This is similar to our static-exchange results, which also lack the long-range potential.

There are several other methods available for calculating shape resonances, among which are the stabilization method,[16] R-matrix method,[17] and close-coupling methods,[18] and many of these methods have been applied to electron-molecule scattering. In its present form, the method used in this work does not lend itself readily to this type of application. The difficulties involved could possibly be circumvented if a procedure could be found for evaluating the needed integrals using Gaussian type functions instead of STO's. The Harris phase-shift method is also not directly applicable to other types of resonances above the excitation threshold and to solve this problem one must use other procedures such as the Harris and Michels minimum-norm method.[9] Nevertheless, for applications to atomic single-particle resonances, we feel that the simplicity of the Harris method outlined in this work makes it very appealing and certainly very competitive with other methods.

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*Present address: Mason Laboratory, Yale University, New Haven, Conn. 06520.

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