

Computation of the position and the width of the $B^- 1s^2 2s^2 2p^2 \ ^1D$ shape resonance

Christos Sinanis, Yannis Komninos, and Cleanthes A. Nicolaides*

Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, 48 Vas. Constantinou Avenue, 116 35 Athens, Greece

(Received 17 November 1997)

State-specific configuration interaction in the continuum calculations, with electron correlation included, shows that shape resonances in polyelectronic atoms can be computed systematically to a high degree of accuracy. Specifically, the $B^- 1s^2 2s^2 2p^2 \ ^1D$ state is computed to be a shape resonance with $E = 95$ meV and $\Gamma = 54$ meV, confirming the tentative identification given recently by Lee *et al.* [Phys. Rev. A **53**, R633 (1996)] for the lowest resonance structure observed in scattering experiments. [S1050-2947(98)50605-1]

PACS number(s): 32.80.Dz, 31.25.-v, 34.50.-s

In a recent Rapid Communication, Lee *et al.* [1] reported experimental energies and widths for the shape resonances of $Li^- (1s^2 2s 2p \ ^3P^o, E_{\text{expt}} = 50 \pm 6$ meV, $\Gamma_{\text{expt}} = 64 \pm 25$ meV) and of $B^- (1s^2 2s^2 2p^2 \ ^1D, E_{\text{expt}} = 104 \pm 8$ meV, $\Gamma_{\text{expt}} = 68 \pm 25$ meV).

As regards the $Li^- \ ^3P^o$ resonance, a recent theoretical study of its structure and decay dynamics produced results in agreement with experiment [2]. With regard to the $B^- \ ^1D$ resonance, Lee *et al.* [1] wrote that they considered its identification tentative and stressed the need for corroboration from reliable calculations. In this context they quoted a result for the energy ($E = 115$ meV) from unpublished work of Froese-Fischer, which agrees with the experimental one. However, no description of this calculation is available and no result for the width is quoted.

The published theoretical results on the E and Γ of the $B^- \ ^1D$ state (see Table I and below) are at variance with the measured values. This is not unusual for an atomic negative-ion (ANI) state such as $B^- 1s^2 2s^2 2p^2 \ ^1D$, whose electronic structure immediately suggests that E and Γ should depend crucially on electron correlation characterizing the localized and the asymptotic parts of the resonance. In fact, even if one, in general, pays attention only to the energy difference between the ANI state and the corresponding bound state of the neutral atom, i.e., the electron affinity (EA), it is necessary for the theoretical approach to be both rigorous and computationally practical (i.e., accounting for interelectronic interactions in the discrete spectrum and in the continuous spectrum), since small errors not only affect the absolute value of the EA but also may change the nature of the ANI state from resonance to a discrete state and vice versa. To support this statement, we give three examples. The first refers to the value of EA of $O^- \ ^2P^o$, a well-established ground-state ANI. Even a huge configuration-interaction (CI) calculation with about 300 000 configurations, using the standard methods of quantum chemistry [3], produced an EA of 1.314 eV, 148 meV smaller than the experimental value of 1.462 eV. The second refers to the $Ca^- 4s^2 4p \ ^2P^o$ bound

state. Until the theoretical [4] and experimental [5] findings a decade ago, it was erroneously calculated to be a shape resonance with a finite width (e.g., [6,7]). The third refers to the possibility of binding an electron by ground-state noble gases. The prediction based on density-functional theory that the noble gases exist as stable negative ions [8] was shown to be erroneous [9].

Published calculations on the nature of the $B^- 1s^2 2s^2 2p^2 \ ^1D$ state and its intrinsic properties can be divided into semiempirical [10–12] and *ab initio* [15,16]. Of these, only the work of Hunt and Moiseiwitsch [12], based on the use of an empirically adjusted model potential (originally employed by Allis and Morse [13]) and on the solution of a one-dimensional Schrödinger equation under scattering boundary conditions, produced the position as well as the width of the resonance (Table I). The other approaches were intrinsically restricted to providing only a value for the energy. The first study was by Johnson and Rohrlich [10], who employed screened Z -dependent perturbation theory and semiempirical extrapolation from ionization potentials. This method produced the result that the $B^- \ ^1D$ state is bound with respect to the $B \ ^2P^o$ ground state by 0.61 eV. Ten years later, Schaefer, Klemm, and Harris [11] analyzed a number of negative ions in terms of particular, state-dependent correlation effects, called “nondynamical correlation” in the Silverstone-Sinanoglu [14] classification and, using empirical data, concluded that “the $B^- \ ^1D$ state does not exist,” since they calculated its energy to be 375 meV above threshold (Table I).

Soon after the Schaefer *et al.* [11] paper, Moser and Nesbet [15,16] published two results on the EA of the $B^- \ ^1D$ state, obtained *ab initio*. They employed the bound-state-type Bethe-Goldstone scheme of CI with all single- and double-orbital [15] or configurational [16] excitations. The first calculation ([15], Table II) showed that the $B^- \ ^1D$ state is essentially on threshold (6 meV above), whereas the second ([16], Table V) showed that it lies 275 meV above. Such a scheme-dependent discrepancy, between two large-scale calculations, demonstrates the difficulty in computing reliably the EA of $B^- \ ^1D$, even without the explicit consideration of the open-channel scattering function space.

In this Rapid Communication we present the results of calculations that accounted for the effects of the self-

*Also at Physics Department, National Technical University, Athens, Greece. Electronic address: can@eie.gr

TABLE I. Energies (eV) with respect to the $B\ 1s^2 2s^2 2p^2 P^o$ ground state and widths (eV) of the $B^- 1s^2 2s^2 2p^2\ ^1D$ shape resonance obtained from various theoretical approaches and from measurements.

	Theory							Experiment
	1959	1969	1970	1971	1972	1996	1997	1996
Reference	[10]	[11]	[12]	[15]	[16]	^a	This work	[1]
E	-0.61	0.375	0.45	0.006	0.275	0.115	0.095	0.104 ± 0.008
Γ			0.11				0.054	0.068 ± 0.025

^aUnpublished result by Froese-Fischer, quoted in Ref. [1].

consistent fields and of electron correlation in the discrete and in the continuous spectrum. These were carried out in the framework of the state-specific configuration interaction in the continuum (CIC formalism and methods [17–20]). In addition, in order to produce results of high accuracy, a systematic extrapolation scheme in conjunction with a series of highly correlated wave functions was tested successfully. Its details will be given elsewhere [21]. Our results show that the $B^- 1s^2 2s^2 2p^2\ ^1D$ state corresponds to a shape resonance with $E = 95$ meV and $\Gamma = 54$ meV, thereby confirming the tentative identification and the values for E and Γ given by Lee *et al.* [1] for the lowest resonance structure.

The strategy of the overall state-specific calculation is the following: First, emphasis is placed on computing the square-integrable part Ψ_0 and the energy E_0 of the 1D resonance, very accurately, in terms of its own function space, by optimizing via energy minimization the zeroth order (multiconfigurational Hartree-Fock) and the correlation part by the nonorthonormal CI methods of the state-specific theory ([22] and references therein). For the L shell, singly, doubly, triply, and quadruply excited configurations were included, with Slater-type orbitals with $n = 3, 4, 5$. The resulting energies for the B^2P^o state were $-24.601\ 70$ a.u. (431 symmetry-adapted configurations), and for the $B^- ^1D$ state were $-24.593\ 99$ a.u. (2892 configurations). The accuracy was improved by applying a systematic extrapolation procedure suitable for negative ions [21]. The final result for L -shell correlation is $E_0(^1D^o - L\ \text{shell}) = -24.596\ 61$ a.u. As regards the energy for the $^2P^o$ state (the threshold), this was obtained by extrapolating to the limit $N \rightarrow \infty$ from the last three values of the energy given in Table II of Ref. [23]. The extrapolated energy for the ground state becomes $E(^2P^o - L\ \text{shell}) = -24.602\ 52$ a.u. Therefore, at this level of calculation, the 1D resonance lies 174 meV above the $^2P^o$ threshold. The K shell, $K-L$ shell, and relativistic effects are estimated, based on the results of Ref. [23] for the $B^- 1s^2 2s^2 2p^2\ ^3P$ affinity, to contribute -5 meV. Therefore, for the bound-state-type calculation, the 1D resonance appears at 169 meV above the boron $^2P^o$ ground state.

The next phase in the overall calculation is the inclusion of the contribution of the remaining part of the continuum to the $B^- ^1D$ state, i.e., the part that was not accounted for during the energy minimization to the local minimum corresponding to the resonance. This is done by first representing the open-channel orbitals, εp and εf , by numerical scattering functions computed in the potential of the multiconfigurational Hartree-Fock (MCHF) core $B\ 1s^2 (0.97\ 2s^2 2p - 0.23\ 2p^3)^2 P^o$. It turns out that, after the CIC, the contribution of the εf channel to the energy shift and width is negligible. Hence, the continuum with which the fully opti-

mized $\Psi_0 (^1D)$ interacts in a quantitatively meaningful manner is $B(2s^2 2p^2 P^o)\varepsilon p\ ^1D$. The value of the resonance position is obtained by solving the equation

$$E = E_0 + F(E) \equiv E_0 + P \int_0^\infty d\varepsilon \frac{W^2(\varepsilon)}{E - E(^2P^o) - \varepsilon}, \quad (1)$$

where P denotes principal value integration and

$$W(\varepsilon) = V(\varepsilon) - ES(\varepsilon) = \langle \Psi_0 | H - E | U(\varepsilon) \rangle, \quad (2)$$

with $U(\varepsilon)$ being the scattering wave function at energy ε . When $V(\varepsilon)$ and $S(\varepsilon)$ are computed systematically and then extrapolated, the position of the 1D resonance is computed to be 96 meV.

Finally, we improved the accuracy by taking into account the effect of the pseudostates arising from the diagonalization of the Hamiltonian in the space of the square-integrable functions [17]. The result is a correction to the shift of only -1 meV. The explanation for this small number is as follows. Because of the overwhelming inclusion of the continuum contributions into Ψ_0 , the interchannel coupling between open and closed channels affected by the inclusion of the pseudostates has an insignificant impact. This result is in accordance with the formal and numerical demonstrations given recently for the cases of widths of resonances [24].

Thus, the combined effect of the self-consistent field and of electron correlation in the discrete and in the continuous spectrum results in the energy position for the $B^- ^1D$ resonance of 95 meV. Finally, the width of the resonance was computed from the formula [17,24]

$$\Gamma = 2\pi \frac{W^2(\varepsilon)}{1 - F'(\varepsilon)}, \quad \varepsilon = E - E(^2P^o), \quad (3)$$

where $F'(\varepsilon)$ is the derivative of $F(\varepsilon)$ defined in Eq. (1). Using the extrapolated matrix elements, the result from Eq. (3) is $\Gamma = 53$ meV. Our final result, including the pseudostates, is $\Gamma = 54$ meV.

It should be stressed that the width of the resonance is very sensitive to the energy of the escaping p electron, since near threshold it behaves like $\Gamma \propto \varepsilon^{3/2}$. Therefore, the calculation of Γ depends crucially on the position of the resonance. This fact provides the justification for developing and applying a sophisticated polyelectronic theory for the reliable computation of shape resonances close to threshold.

- [1] D. H. Lee, W. D. Brandon, D. Hanstop, and D. J. Pegg, *Phys. Rev. A* **53**, R633 (1996).
- [2] Th. Mercouris and C. A. Nicolaides, *J. Phys. B* **30**, 811 (1997).
- [3] D. Feller and E. R. Davidson, *J. Chem. Phys.* **90**, 1024 (1989).
- [4] C. Froese-Fischer, *Phys. Rev. A* **39**, 963 (1989).
- [5] D. J. Pegg, J. S. Thompson, R. N. Compton, and G. D. Alton, *Phys. Rev. Lett.* **59**, 2267 (1987).
- [6] C. W. McCurdy, J. G. Lauderdale, and R. C. Mowrey, *J. Chem. Phys.* **75**, 1835 (1981).
- [7] H. A. Kurtz and K. D. Jordan, *J. Phys. B* **14**, 4361 (1981).
- [8] Y. Guo, M. C. Wrinn, and M. A. Whitehead, *Phys. Rev. A* **40**, 6685 (1989).
- [9] C. A. Nicolaides and G. Aspromallis, *Phys. Rev. A* **44**, 2217 (1991).
- [10] H. R. Johnson and F. Rohrllich, *J. Chem. Phys.* **30**, 1608 (1959).
- [11] H. F. Schaefer III, R. A. Klemm, and F. E. Harris, *J. Chem. Phys.* **51**, 4643 (1969).
- [12] J. Hunt and G. L. Moiseiwitsch, *J. Phys. B* **3**, 892 (1970).
- [13] W. P. Allis and P. M. Morse, *Z. Phys.* **70**, 567 (1931).
- [14] H. J. Silverstone and O. Sinanoglu, *J. Chem. Phys.* **44**, 1899 (1966); **44**, 3608 (1966).
- [15] C. M. Moser and R. K. Nesbet, *Phys. Rev. A* **4**, 1336 (1971).
- [16] C. M. Moser and R. K. Nesbet, *Phys. Rev. A* **6**, 1710 (1972).
- [17] Y. Komninos, G. Aspromallis, and C. A. Nicolaides, *Phys. Rev. A* **27**, 1865 (1983).
- [18] Y. Komninos and C. A. Nicolaides, *Z. Phys. D* **4**, 301 (1987).
- [19] Y. Komninos, G. Aspromallis, and C. A. Nicolaides, *J. Phys. B* **28**, 2049 (1995).
- [20] Ch. Sinanis, Y. Komninos, and C. A. Nicolaides, *Phys. Rev. A* **51**, R2672 (1995).
- [21] Ch. Sinanis, Y. Komninos, and C. A. Nicolaides (unpublished).
- [22] C. A. Nicolaides, *Int. J. Quantum Chem.* **60**, 119 (1996).
- [23] C. Froese-Fischer, A. Yunker, and G. Gaigalas, *Phys. Rev. A* **51**, 4611 (1995).
- [24] C. A. Nicolaides, N. Piangos, and Y. Komninos, *Phys. Rev. A* **48**, 3578 (1993).