

Comments on the existence of low-energy d -wave resonances in electron-fluorine atom scattering*

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It is argued that the very narrow, low-energy ${}^1D^o$ and ${}^1P^o$ d -wave shape resonances in the e^- -F system reported by Ormonde must be artifacts. Evidence that this is so is drawn from numerical Hartree-Fock calculations, from construction of effective local potentials, from calculations with model polarization potentials, and from extensive configuration-interaction/stabilization computations. No evidence of such resonance behavior is found in any of these calculations.

Multiconfiguration close-coupling calculations on the e^- -F system have been reported recently by Ormonde,¹ which show the existence of extremely narrow ${}^1P^o$ and ${}^1D^o$ d -wave shape resonances very close to the elastic threshold. These resonances, if confirmed, would lead to very large near-threshold values of the electron- and photon-detachment cross sections of F^- and could possibly effect the energy deposition rates in electron-beam-pumped H_2/F_2 and rare-gas/ F_2 mixtures.

Normally, the introduction of an electron into the lowest vacant valence orbital of most elements leads to a stable negative ion. For this reason, shape resonances, which are generally associated with an unbound or virtual state, are extremely rare in elastic e^- -atom scattering.² Notable exceptions are the elastic p -wave shape resonances in the group IIA and B atoms, which have recently been seen experimentally.³ The fluorine atom ($2p^5, {}^2P^o$) fits the usual pattern, where the addition of an extra electron leads to a stable negative ion ($2p^6, {}^1S^e$). While the existence of this negative ion does not preclude a shape resonance with $l > 1$, such a resonance (elastic d -wave) has never been seen until now.

Recent *ab initio* calculations of the photodetachment of F^- by Rescigno, Bender, and McKoy⁴ and also other investigators⁵ showed no evidence of such a low-energy ${}^1P^o$ resonance. For this reason, we decided to carry out further investigations on this system in order to see if Ormonde's findings could be substantiated. As we will show, various arguments can be made which suggest that sharp d -wave resonances at ultralow energies ($\sim 4 \times 10^{-4}$ a.u.) are extremely unlikely. We have performed a number of calculations of different varieties, all of which gave no sign of a physical resonance.

In the case of the ${}^1D^o$ symmetry, there is only one possible elastic channel—($2p^5kd$). We therefore carried out numerical Hartree-Fock (HF)

calculations for the kd orbital in this case, using a code written by Bates.⁶ The bound orbitals used in these computations were Clementi's⁷ self-consistent-field (SCF) orbitals for ground-state fluorine. Elastic d -wave phase shifts were obtained over a very fine mesh of energies (1.0×10^{-5} a.u.) between 3.0×10^{-4} and 5.0×10^{-4} a.u. No rapid variations in the phase shifts were found, and the wave functions were not localized. We did note that, at these low energies, the extremely small phase shifts (~ -0.0004 rad) are rather sensitive to the step size and range used in the numerical integrations.

We also performed numerical HF calculations for the ($2p^5kd$) ${}^1P^o$ states over the same energy range. No resonances were found. However, for this symmetry, the elastic channel ($2p^5ks, {}^1P^o$) is also allowed and the possible coupling between the two channels should be considered. We did not have access to a numerical close-coupling code, but we did address the coupling in another series of calculations which we will discuss later.

It can be argued that at such low energies, the electron is effectively scattering off the tail of the long-range centrifugal potential and the Born approximation for the phase shift

$$\delta_l \approx -k \int j_l(kr)U(r)j_l(kr)r^2 dr \quad (1)$$

should be valid. Thus the magnitude and sign of the phase shift should be determined by the tail of the potential. For the ${}^1D^o$ and ${}^1P^o$ multiplets, the coefficients of the long-range, direct part of the Hartree-Fock potential (see Ref. 8) have the same numerical value, but differ in sign. Indeed, our computed phase shifts for ${}^1P^o$ and ${}^1D^o$ differed only in sign over the energy range considered. This implies that a d -wave resonance could be found only in one of the two cases. Yet Ormonde reports resonances in the same energy range for both symmetries.

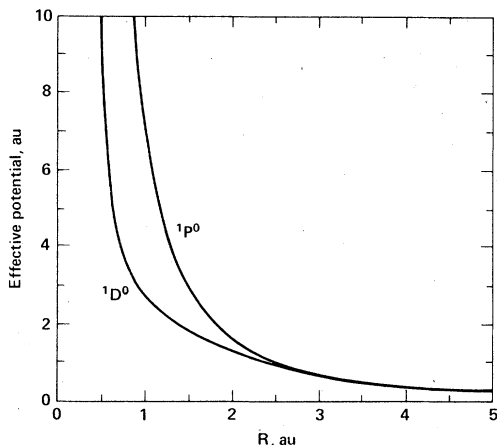


FIG. 1. Effective local potentials for a low-energy continuum *d* orbital in the configurations $(2p^5kd)1P^0$ and $(2p^5kd)1D^0$.

The formation of a “shape” resonance is generally associated with an effective potential which has a barrier through which an electron can tunnel. The combination of a sufficiently attractive potential and a repulsive centrifugal term leads to a potential well which can temporarily bind an incoming electron. The fact that the HF operator has nonlocal exchange terms, however, prevents one from rigorously defining such a local effective potential. Nevertheless, one can obtain an effective, energy-dependent, local potential from the wave function through the prescription⁹

$$U_{\text{eff}}(r) = \frac{d^2\psi(r)/dr^2}{\psi(r)} + k^2. \quad (2)$$

At low energies, the first node in the wave function appears at a large enough value of r to make the construction of Eq. (2) straightforward. This potential will obviously reproduce the correct phase shifts. Such potentials were constructed for the $1P^0$ and $1D^0$ cases from our computed wave functions and were found to be virtually energy independent over the incident electron energy range 0.0003–0.01 a.u. They are shown in Fig. 1. As can be seen, these effective potentials are purely repulsive and offer further proof for the nonexistence of *d*-wave shape resonances.

The calculations described so far have ignored polarization effects. It might be argued that inclusion of such effects would lead to an increased attraction of sufficient strength to allow for the formation of a local minimum in the effective potential. A simple, often used, but nonrigorous way to account for this effect is through the introduction of a local polarization potential. The $1D^0$

calculations were thus repeated with the addition of a term

$$V^{\text{Pol}}(r) = -\alpha/(r^4 + r_c^4) \quad (3)$$

to the HF potential. The cutoff parameter r_c was chosen to be 5 a.u., which corresponds to a value slightly greater than the range of the atomic charge distribution. No resonances were obtained when the correct value for the polarizability of atomic fluorine was used for α .¹⁰ This situation remained unchanged even when the cutoff parameter was decreased to 1.0 a.u., an unusually small value. However, by varying the value of α (for $r_c = 5$ a.u.), we were able to produce a very narrow ($\Gamma = 2.4 \times 10^{-4}$ a.u.) *d*-wave resonance at an energy of 2.4×10^{-3} a.u., but not until α had been increased to 235 a.u. which is some 65 times larger than the true static polarizability of fluorine. This is clearly unphysical.

Finally, we performed extensive configuration-interaction calculations on the $1D^0$ and $1P^0$ states of F^- and looked for some evidence of stability in a low-energy *d*-wave solution.¹¹ The configurations were constructed from linear combinations of normalized Slater-type orbitals. For these calculations, basis sets containing up to 14*s*, 4*p*, 10*d*, and 1*f* Slater functions were used. The large number of *s* and *d* functions were included in order to be able to describe low-energy *s*- and *d*-wave continuum orbitals over a considerable range of coordinate space. The *d* basis was carefully chosen to include both tight and diffuse functions, so that both localized resonant behavior, as well as low-energy nonresonant behavior, could be accounted for.

For the $1D^0$ calculation, we included, in addition to the elastic $(2p^5nd)$ configurations, correlating configurations of the type $(2s\bar{s}2p^5nd)$, $(2s\bar{d}2p^5nd)$, $(2s^22p^4\bar{p}nd)$ and $(2s^22p^4\bar{f}nd)$. The \bar{s} , \bar{p} , \bar{d} , and \bar{f} orbitals are correlating atomic orbitals chosen to have the same spatial extent as the 2*s* and 2*p* occupied orbitals. For the $1P^0$ calculations, an analogous set of configurations with *nd* replaced by *ns* were also included. The *d*-orbital exponents were varied, but in each case it was found that the lowest-energy solutions obtained were determined by the most diffuse *d* orbital included in the basis; there was no sign of stability. Furthermore, a natural orbital analysis of the low-energy solutions showed that the eigenfunctions were completely nonlocalized, which is most uncharacteristic of a resonance.¹¹

We feel that we have accumulated a sufficient body of evidence to suggest that the proposed *d*-wave shape resonances are artifacts. It is likely that Ormonde’s findings are due to either a nu-

merical instability or some new and unusual physical effect. However, only analogous close-coupling calculations by other investigators can verify this conclusion with complete certainty.

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¹¹See, for example, A. U. Hazi and H. S. Taylor, *Phys. Rev. A* **1**, 1109 (1970); H. S. Taylor, *Adv. Chem. Phys.* **18**, 91 (1970); H. S. Taylor and A. U. Hazi, *Phys. Rev. A* **14**, 2071 (1976).