Effects of Shape Resonances in the Spectra of Negative Ions

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Abstract

This paper includes theoretical investigation of two major effects of shape resonances in the spectra of atomic negative ions. The localization effect of a shape resonance in the core of the parent neutral atom maintains stable width of the resonance against external moderate electric and magnetic fields. The binding energy effect establishes a simple connection rule between two different processes involving iso electronic systems such as photodetachment and electron-atom scattering.

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Introduction

A shape resonance is a quasibound state of a particle in which it is temporarily trapped by a potential barrier through which it may eventually tunnel and escape. The name of the resonance implies that its behavior arises from the shape of a local potential barrier.

The earliest shape resonance in photoabsorption spectra was observed in 1966 in gaseous SF6 (Villa and Deslattes, 1966), but no interpretation was given at that time until 1972 (Dehmer, 1972). Since then, there has been great progress and expanding interest in shape resonant phenomena. At the present time, shape resonances in many neutral molecules are known but only a few are known in the spectra of negative ions. The mechanism of shape resonances in the quantum mechanical picture reveals interesting effects that motivate both theoretical and experimental investigation or well-established confirmation.

In this paper, the effects of shape resonances are investigated in the spectra of negative ions through both negative ion-beam experiments and electron-atom or molecule scattering techniques.

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Theory

The basic shape resonance mechanism is presented in Fig.1 (Child, 1974), where both the wave function of the electron $\Psi(r)$ and the effective potential $V(r)$ are plotted as a function of radial distance $r$ using electron energies: below resonance $E<E_r$, at resonance $E=E_r$, and above resonance $E>E_r$. The potential barrier is the repulsive centrifugal barrier given by the relation (Gasiorowicz, 1974):

$$V(r) = \left[ l(l+1) \frac{\hbar^2}{2\mu r^2} \right] + V_s \quad (1)$$

where $l$ is the orbital angular momentum of the electron and $\mu$ is its reduced mass. The potential energy function $V(r)$ has an inner well at small radial distances formed by the partially screened nuclei in the molecular core. Therefore, it is highly anisotropic and overlaps much of the molecular charge distribution. At resonance ($E=E_r$), the inner well supports a quasibound state where the radial wave function $\Psi(r)$ is essentially an eigenfunction of the inner well. At energies below the resonance energy ($E<E_r$), the antinode of the radial wavefunction penetrates the potential barrier towards the inner well suffering a rapid increase of $\pi$ radians in phase shift. Thus the amplitude of the radial wavefunction is greatly enhanced in the inner well over a narrow band of energy near $E_r$ although it decays through the barrier. Similarly, at $E>E_r$ the wavefunction becomes an eigenfunction of the outer well only. The single-particle nature of shape resonances stimulates theoretical treatment by realistic independent electron methods introduced by several researchers to improve the fundamental conceptual work based on atomic orbitals. The multiple-scattering method (MSM) (Dehmer, Siegel, Welch, and Dill, 1980) uses a potential model for molecules that consists of nonoverlapping spherical potentials centered on the individual atomic sites. The zero-core-contribution method (ZCCM) (Clodius, Stehman, and Woo, 1983) assumes that the wave function of the atomic core remains unchanged during the photodetachment of any atomic or molecular negative ion.

The shape resonance of the simplest negative ion, $\text{H}^-$, was experimentally observed for the first time in a photodetachment experiment in 1977 (Bryant, et.al. 1977; Gram, et.al, 1978) using relativistic kinematics of an 800-MeV ion beam crossed at a variable angle with a nitrogen laser beam. The resonance energy was
10.98 eV lying above threshold for the excited state of the atom H(n=2) and its full width at half maximum (FWHM) was about 25 meV. The effect of an external electric field on both the resonance energy (E) and the FWHM (Γ) was investigated experimentally (Gram, et.al, 1978; Comtet, et.al, 1987; Williams, 1988) and theoretically (Broad and Reinhardt, 1976; Ning-Yi, Fabrikant, and Starace, 1993; Ho and Bhatia, 1993; Ho, 1998).

Assuming short-range potential in the electron-atom scattering problem, the partial wave cross section is (Massey, 1976; Massey, 1979; Burke, 1977):

\[ \sigma_L^r = (4\pi / k^2) (2L + 1) \sin^2 [\delta_L^0(k) + \delta_L^r(k)] \]

(2)

Where \( L \) is the total angular momentum of the resonant state, \( \Gamma \) is the full width of the resonance peak at half maximum (FWHM), \( \delta_L^0(k) \) is the background phase shift, and \( \delta_L^r(k) \) is the resonant phase shift given by the relation:

\[ \sigma_L^r = (4\pi / k^2) (2L + 1) \sin^2 \delta_L^r(k), q + \kappa^2 / (1 + \kappa^2) \]

(3)

\[ \delta_L^r(k) = \tan^{-1} \left[ \left\{ (\Gamma / 2) \right\} / (E_r - E) \right] \]

(4)

\[ \kappa = (E - E_r) / (\Gamma / 2) \]

and \( q = \cot \delta_L^0(k) \)

(5)

q is the line profile index or resonance shape parameter.

The total cross section (\( \sigma \)) can be written as:

\[ \sigma = \sigma_0 + \sigma_L^r \]

(6), where

\[ \sigma_0 = (4\pi / k^2) \sum_{l=L} (2l + 1) \sin^2 \delta_L^0(k) \]

(7), or:

\[ \sigma = \sigma^B + \sigma_L^0[(q^2 + 2q \kappa - 1) / (1 + \kappa^2)] \]

(8), where:

\[ \sigma_L^0 = (4\pi / k^2) (2L + 1) \sin^2 \delta_L^0(k) \]

(9)
\( \sigma^0_L \) is the partial cross section for angular momentum \( L \) in the absence of resonance. Since \( \sigma^0 \) is expected to vary smoothly and gradually with electron energy \( E \), then the resonance effect is determined by the function:

\[
\frac{\left(q^2 + 2q \varepsilon - 1\right)}{\left(1 + \varepsilon^2\right)}
\]

**Results**

1- Localization effect:

The eigenfunctions of the negative ion are localized inside the potential barrier being substantially uncoupled from the external environment of the atom or molecule.

Both experimental (Gram, et.al, 1978; Comtet, et.al., 1987; Williams, Phys, 1988) and theoretical (Broad and Reinhardt, 1976; Ning-Yi, Fabrikant, and Starace, 1993; Ho and Bhatia, 1993; Ho, 1998) investigations on \( \text{H}^- \) confirm that the width of the shape resonance is unaffected by externally applied electric fields of moderate values up to a value of 240 kV/cm.

This effect shows that the external electric field affects the asymptotic behavior of the effective potential on the outer edge where it decreases as \( r^{-2} \) while the the potential barrier stays unaffected on its peak and inner edge (Comtet, et.al., 1987). The Fano profile fit to the photodetachment cross-section in eq.(8) yields an asymmetry parameter \( q=5.5 \pm 0.2 \) with FWHM \( \Gamma =22.2 \pm 0.6 \) meV. The resonance asymmetry is due to slow decrease in slope of the potential energy curve above \( n=2 \) threshold. The potential barrier height relative to \( \text{H} (n=1)+e \) given by eq.(1) is 65 meV.

However, strong external electric fields would increase the energy of other nonlocalized Feshbach resonance peaks which lie below threshold in the field-free case. This shift towards the higher energy side of such Feshbach resonances introduces strong interference with the shape resonance causing an increase in the width of the compound resonance peak as the external electric field increases further.

This interpretation supports the persistence of the localized nature of the shape resonance even under strong electrostatic effects while other types of resonances are nonlocalized even in the absence of any electrostatic or even electromagnetic perturbations.
2- Binding energy effect:

The electron affinity (EA) of an atom or molecule (M) is the difference between the total energies \( E_{\text{tot}} \) of the ground states of M and its negative ion \( M^- \):
\[
EA(M) = E_{\text{tot}}(M) - E_{\text{tot}}(M^-) \tag{10}
\]
This quantity is positive for stable negative ions and it represents the binding energy of the extra electron.

The localized nature of a shape resonance maintains its identity in different atomic or molecular processes involving isoelectronic systems such as photodetachment of a negative ion and electron-atom or molecule scattering. The photodetachment of a negative ion produces a "complex" system that leads to a final state of a free electron and a neutral atom or molecule,
\[
h\nu + M \rightarrow (M^-)^* \rightarrow M + e \tag{11}
\]
In an electron-atom or molecule scattering a "complex" system is formed, i.e.,
\[
e + M \rightarrow (M^*) \tag{12}
\]
The photodetachment cross section for the process of eq.(11) is measured as a function of photon energy \( h\nu \) while the scattering process of eq.(12) involves measurement of cross section as a function of the kinetic energy of the incident electrons (K.E.).

The difference (shift) in energy for a shape resonance peak connecting the two processes is equal to the binding energy of the extra electron in the negative ion or the electron affinity (EA) of the neutral atom or molecule (M).

One example of this effect is the shape resonance of \( H^- \) above the \( H(n=2) \) threshold where it appeared in the photodetachment spectrum of \( H^- \) at a photon energy \( h\nu = 10.98 \pm 0.006 \text{ eV} \) (Gram, et.al, 1978; Comtet, et.al, 1987) as shown in Fig.2.

The same shape resonance was observed in an inelastic scattering experiment between electrons and \( H \) atoms where the cross section revealed a shape resonance peak at a kinetic energy of electrons K.E. = 10.217 \( \pm 0.003 \) eV (Williams, Phys, 1988) as shown in Fig.3. In fact, the same resonance peak appeared in an earlier scattering experiment with lower energy resolution (Schulz, 1973) as shown in Fig.4. The difference (shift) in energy of the shape resonance is \( 0.763 \pm 0.007 \text{ eV} \), exactly equal to the binding energy of the electron in \( H^- \) or the electron affinity of \( H \) atoms within the margin of experimental uncertainty. The value of the binding energy in \( H^- \) tabulated in Ref. (Hotop and Lineberger, 1985) is 0.754209(3) eV from theoretical calculations, which is very close to the energy shift obtained through connection between two different experimental determinations of the same shape resonance in two different processes.
The rule for this effect can be formulated in a simple relation as follows:-(13)

\[(hv)_{pd} - (K.E.)_{sc} = EA\]

where pd stands for photodetachment process and sc for scattering process.

Conclusion:

The theoretical investigation of shape resonance effects in the spectra of negative ions leads to two well-established effects:

1- Localization effect maintains stable width of the shape resonance against external electric and magnetic fields.

2- Binding energy effect establishes a connection rule for a shape resonance between two different physical processes such as photodetachment and scattering.

Although the investigation was mainly restricted to atomic negative ions, future work on molecular negative ions would test the Frank-Condon principle and the Wigner threshold law.

The limitations at the present time are mainly due to the limited scanning range of lasers and the difficulties in the experimental work involving photodetachment techniques.

أتار الرنين الهيكلي في أطياف الأيونات السالبة

محمد العبادي
ملخص

تتضمن هذه الورقة البحثية دراسة نظرية لأثيرين رئيسيين من أثار الرنين الهيكلي في أطياف الأيونات السالبة. يحافظ الأثير الموضعي للرنين في لب الذرة الأم المتعادلة على اتزان عرضه ضد المجالات الكهربائية والمغناطيسية متوسطة الشدة. كما يبني أثيرما طاقة بربط قاعدة ارتباط بسيطة بين عمليتين مختلفتين لنظامين ألكترونيين متشابهين مثل عملية تحرير الإلكترون الإضافي بوساطة فوتون وعملية تشتيت الإلكترونات بفعل الذرات.
References

Fig. 1: Wave functions of an excited electron for three different energies: (a) $E > E_r$, (b) $E = E_r$, and (c) $E < E_r$, where $E_r$ is the resonance energy. The wave function at resonance ($E = E_r$) is reduced by a factor of one-tenth for comparison with the off-resonance cases. The dotted curves represent the potential energy $V(r)$ shown as a function of radial distance ($r$) of the electron measured from the center of the atom or molecule in Bohr radius units ($a_0$).
Fig. 2: The photodetachment experiment [9] using 800-MeV H⁻ beam and nitrogen laser beam crossed at a variable angle 20 deg. ≤ θ ≤ 160 deg. The shape resonance peak has a photon energy of $10.980 \pm 0.006$ eV with a full width at half maximum $\Gamma = 23 \pm 6$ meV.
**Fig. 3:** Inelastic scattering experiment [11], showing the 2p excitation cross section ($\sigma$) as a function of the incident electron energy. The 1p shape resonance peak is located at K.E.=10.217 ± 0.003 eV with a full width at half maximum $\Gamma = 22 \pm 3$ meV.

**Fig. 4:** Inelastic scattering experiment [19], showing the total scattering cross section of hydrogen atoms as a function of the K.E. of incident electrons. The shape resonance peak occurs at a K.E. of 10.25 ± 0.07 eV.