Bound and Quasi-Bound States in the Continuum

One-dimensional models of square-integrable states embedded in continua, first offered by von Neumann and Wigner, can stabilize ordinary resonance levels and have gained importance in connection with solid state heterostructure semiconductor devices. General continuum bound state theories for many-particle systems do not exist, but models for continuum crossings of bound states suggest possible long-lived states, including some double charged anions. Nonlinear variational calculations can provide estimates of resonance energies and of the rapid onset of instability in various atomic and molecular ionization phenomena, typifying results found in mathematical "catastrophe theory".

One-Dimensional Models

Many years ago von Neumann and Wigner[1] pointed out that local potentials could have bound (i.e. square-integrable) eigenstates with positive energies. These states are embedded in the continuum of scattering states with the same symmetry, but nevertheless would fail to "ionize". Thus it would be proper to regard these continuum bound states as infinitely sharp resonances.

The example offered by von Neumann and Wigner (subsequently corrected by Simon[2]) was one-dimensional, and involved an oscillatory potential $V(x)$ which behaved essentially as $(\sin x)/x$ for large $|x|$. Likewise the square-integrable wavefunction $\psi(x)$ for the positive energy bound state was oscillatory but, owing to diffractive interference induced by $V(x)$, the amplitude of ψ was driven toward zero as $|x|$ increased, so that particle binding resulted. The existence of this elementary example naturally raises questions about whether similar continuum bound states could exist in physically more realistic cases.

There have been several subsequent extensions of the von Neumann-Wigner work. Weidmann[3] constructed a family of discontinuous (but bounded) potentials which produced continuum bound states. Furthermore, Moses and Tuan,[4] using Gel'fand–Levitan theory, have produced a local potential which not only has a positive energy eigenstate, but for which the scattering states have been explicitly calculated in closed form. Stillinger and Herrick[5] have constructed

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further examples, and in particular show that a potential can be analytically varied so as to carry a conventional bound state smoothly up into the continuum, to become an embedded bound state. At least with respect to one-dimensional examples, it is easy to show that any $V(x)$ which supports a continuum bound state *must* be oscillatory, and can drop off to zero with increasing $|x|$ no faster than $|x|^{-1}$.

It has recently been pointed out[6] that epitaxial heterostructure semiconductor devices may offer a way to achieve potentials with continuum bound states. Using the technique of molecular beam epitaxy, alternating layers of GaAs and $Al_xGa_{1-x}As$, each several monolayers thick, can be grown by periodically varying the mole fraction of Al.[7] An electron moving across these heterolayers sees an effective one-dimensional potential consisting of a sequence of rectangular barriers and wells, due to a mismatch of the conduction band edges of the doped and undoped regions, respectively. For multiple, evenly spaced barriers the heterostructure potential has the form of a one-dimensional periodic "superlattice".[8] The oscillations in the potential provide a means for constructing a bound state in the continuum as the number of barriers approaches infinity. If the potential is cut off at a finite range (i.e. $V(x) = 0$ for $|x| > L$), the initial continuum bound state is perturbed and decays to the adjacent continuum. This quasi-bound state appears as a sharp peak in the computed transmission spectrum for incident electrons. The resonance width can be made arbitrarily small by adding more barriers to the ends of the potential according to the theoretical prescription for continuum bound states. This behavior is evident even for potentials containing a few barriers, as shown in Figure 1. In this example the distance between individual barriers is held constant but the heights and widths vary as the number of barriers increases. For the case illustrated the resonance energy remains unshifted as more barriers are added, and is isolated much as a defect state for a periodic lattice is isolated within a band gap. On account of its isolation, the peak has a nearly perfect Breit-Wigner shape. The heights of subsequent barriers converge towards zero, and the overall transmission spectrum will deviate from that of a periodic lattice. Some model potentials having fewer than 100 barriers predict decay lifetimes as long as 1 second. Modifications of the theory which admit multiple, nondegenerate bound states have also been devised,[9] and experiments making use of these theories may lead to laser applications.

Many-Particle Systems: Continuum Crossings

While the stability of the one-dimensional models is easily understood, conditions for the formation of possible bound states in the continuum for many-electron and molecules are unknown. For E below the first ionization threshold, E_1, the nonrelativistic electronic energy spectrum is discrete. The zero of energy corresponds to the removal of all electrons to infinity. It is easy to show[10,11]

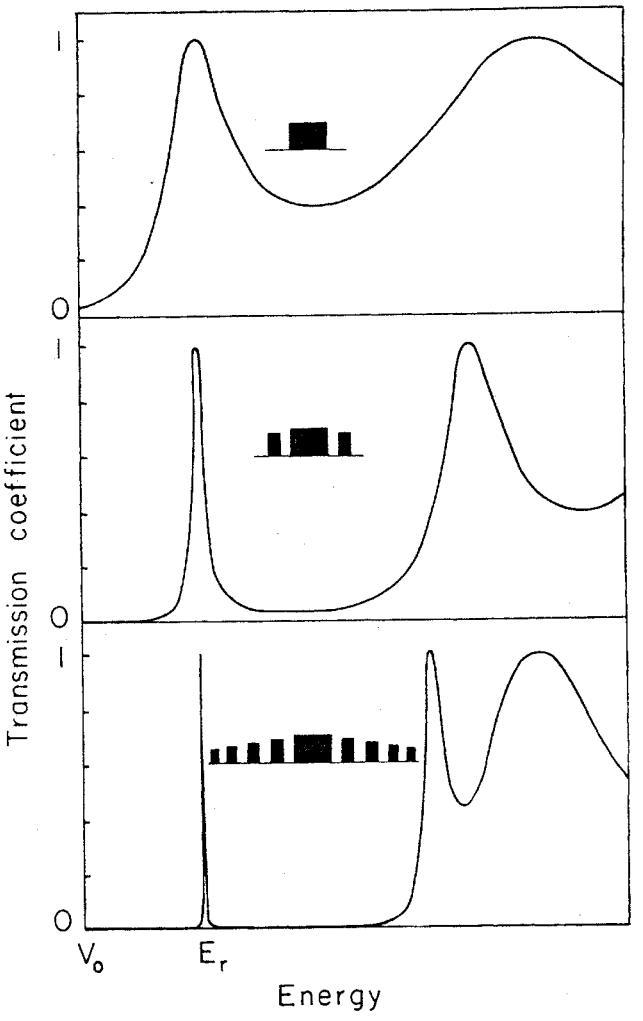

FIGURE 1. Transmission spectra for three symmetric "heterostructure" potentials for incident electron energies above the central barrier V_0. Diffractive interference sharpens the peak at E_r as more barriers are added according to continuum bound state theory. (The authors thank Mr. P. Wong for assistance in computing these spectra.)

that no bound states exist for $E > 0$, since the virial theorem cannot be satisfied in this region. However, there is no analogous proof for the nonexistence of

bound states in the intermediate continuum regions, $E_1 < E < 0$. There are obvious examples of bound states above threshold (e.g. $2p^2\ ^3P$ for He), but these lie in continua having different symmetry.

It is possible that a continuum bound state might not have a simple description in terms of the usual atomic or molecular configurations, owing to a delicate balance of many-particle correlations. This circumstance would make even theoretical detection difficult by computational techniques involving electron orbitals and finite configuration interactions. Neglecting the occurrence of such an anomalous state, we consider instead a Hamiltonian $H(\lambda)$ which has a well-defined discrete spectrum for some range of values of the parameter λ. By varying λ it is possible for an isolated bound state eigenvalue to enter a continuum of states. In Figure 2 a bound state E_o lies below the threshold E_1 for $\lambda < \lambda_c$, but rises up into the continuum for $\lambda > \lambda_c$, where it becomes a resonance state.

The behavior of the continuum crossing for radial potentials having repulsive $1/R^2$ tails is well-understood, being central to ordinary resonance scattering theory.[12] For instance, λ might represent the rotational angular momentum barrier in a low energy atom-atom collision on an attractive potential energy curve. The resonance corresponds to a transient vibrational mode below the top of the centrifugal barrier for angular momentum J; dissociating via barrier tunneling. The identical states can be excited in electronic spectra of diatomics, although predissociation by rotation is significant primarily for hydrides.[13] From a bound state viewpoint each energy level (and wavefunction) below threshold can be analytically continued around a singularity at λ_c to energies above threshold, by continuously increasing the value of λ. The resulting energies are complex, $E_o = E_r \pm i\Gamma/2$ due to a nonhermitian boundary condition for the analytically continued wavefunction. At $E_r - i\Gamma/2$ the wavefunction has the pure outgoing current associated with a decaying state, and for small Γ this state appears as a resonance (of width Γ) in the scattering cross section at energy E_r. Similar analyses are possible for other barrier potentials, although the precise nature of the threshold singularity in terms of λ may differ in each case.

We have seen that appropriate oscillations in a one-dimensional potential $V(x)$ can cause arbitrary increases in lifetime of what might otherwise be a simple tunneling resonance. Another phenomenon apparently exists as well which can also increase resonance state lifetimes, but it operates only in non-separable multidimensional systems. That such an independent mechanism could exist was implied by a doubly excited He atom model proposed by Stillinger and Herrick,[5] with suitable interaction between its electrons, which possessed infinite lifetime.

This second mechanism has its origin in the striking nonergodic behavior that is known to exist for nonseparable classical dynamical systems. Systems of coupled oscillators, for example, can behave as though action-angle variables

continued to exist even when nonlinear perturbations are present.[14] The result is that the dynamical system fails to cover the full constant-energy surface that in principle is available to it. In the case of several interacting particles orbiting a center of attraction, this nonergodic behavior can have the effect of preventing the system from discovering a dissociation channel. Our own nine-planet solar system may provide an example of this behavior, for in spite of the fact that sufficient energy is available to eject one of the planets, indefinitely long-term stability of the present bound configuration seems to prevail.

Quantum mechanical implications of this nonergodicity are largely unexplored. Even the underlying classical theory is complicated and incomplete.[15] Nevertheless we can reasonably expect that the lifetimes of planetary systems of electrons orbiting nuclei can be substantially increased under the proper conditions. It seems likely, therefore, that the width of a resonance state might be extremely small – or even vanish – for some values of λ.

Doubly Charged Anions

For atomic isoelectronic series one has $\lambda = 1/Z$, and the nonrelativistic bound state has a simple hydrogenic form in the limit $\lambda = 0$. The He-like atoms have been studied extensively[16] for continuous values of λ, although the continuum penetration region lies outside the range of physical atomic species H^-, He, Li^+, . . . However, an N-electron isoelectronic sequence having a bound negative ion at $\lambda = (N-1)^{-1}$ correlates with multiply charged anions at higher values of λ. Specific examples of doubly-charged anion sequences include the ground states of (Ne, F^-, O^{2-}), (Ar, Cl^-, S^{2-}), and the corresponding states for Se^{2-} and Te^{2-}. The O^{2-} level was predicted[17] to lie 5.38 eV above the $O^- + e^-$ threshold, with an estimated width of 1.3 eV. It is possible that doubly-charged anions which lie closer to threshold may have extremely narrow widths.

The proposed stability for these resonances has a simple interpretation. The ejected electron sees a long-range Coulomb repulsion, whereas binding dominates closer to the nucleus. This combination can produce an extremely thick barrier which severely inhibits tunneling – more so than in the resonances involving repulsive centrifugal barriers. Extensive analyses of isoelectronic species in the light of the continuum penetration model may provide simple explanations for the wide variety of long-lived doubly-charged anions observed experimentally.[18-21] As pointed out in Ref. 17, ordinary fitting formulas such as Edlen's for empirical isoelectronic energies do not account for the development of a tunneling width when $\lambda > \lambda_c$.

The continuum crossing in Figure 2. is "hard" in the sense that E_o enters the continuum sharply at λ_c, and interacts with no other states. There is a second type of crossing, shown in Figure 3, which by comparison is "soft". Here a single level E_o rises into the continuum after passing through a Rydberg series of states which themselves represent a quasi-continuum. The "avoided

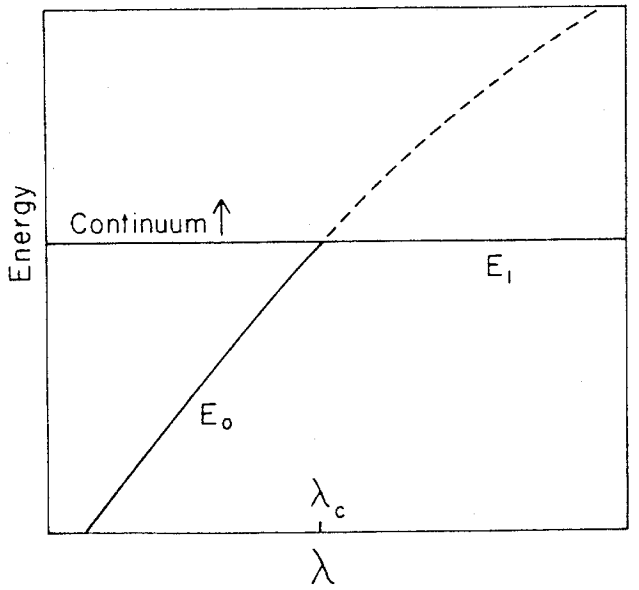

FIGURE 2. Schematic representation of a continuum crossing. Bound state E_0 rises above threshold E_1 as a potential energy parameter λ is varied.

crossings" below threshold produce a shift in the quantum defect for the Rydberg series. Above threshold ($\lambda > \lambda_c$) this shift corresponds to a resonant scattering phase shift for the continuum wavefunction. A crossing of this type occurs in the Be isoelectronic sequence, where the doubly-excited $2p^2\ ^1S$ state rises up through the single excitation series 2sns as λ increases. At Be ($\lambda = 1/4$) the $2p^2$ level is thought to lie less than 1 eV above the first ionization threshold.[22,23] The higher 2pnp levels experience a similar fate.

An analogous mechanism explains the correlation of doubly-excited $2s2p\ ^1P$ He from below the second ionization threshold [He^+ (n=2) + e^-] to the narrow shape resonance just above threshold at 10.22 eV in H^-.[24] In this case the infinite series of states has a group theoretic "configuration mixing quantum number" $K = +1$ as described by Herrick and Sinanoglu.[24,25] The 2s2p level, on the other hand, has $K = 0$. As these examples indicate, the soft continuum crossings involve multichannel couplings. Examples of continuum bound states in systems of coupled Schrödinger equations (i.e., nonlocal potentials) were

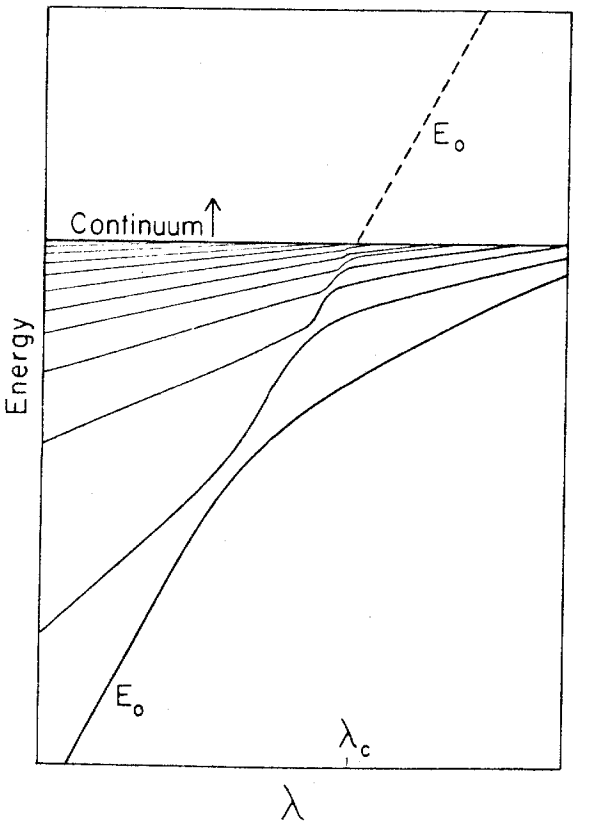

FIGURE 3. A "soft" continuum crossing. Bound state E_0 enters the continuum via a series of avoided crossings with a Rydberg series below threshold. The sharp crossing in Figure 2 is "hard" by comparison.

described by Fonda and Newton.[26]

Catastrophic Instabilities

Although continuum crossings provide a means for the identification of states which might exhibit stability against ionization, there exists at present no firm evidence for an experimentally observable continuum bound state. Reinhardt,[27] using theories of dilation-analytic operators[28,29] has argued that the occurrence of a zero-width bound state via a continuum crossing is unlikely. However, the

mathematical question about whether $E_o(\lambda)$ is singular precisely at encounter with the continuum ($\lambda = \lambda_c$) in many cases may be exceedingly difficult to answer. At the same time, the exact answer may have little direct experimental significance. For any Stark (electric) field applied to the atom, for example, we know that a nonzero tunneling probability exists for electron escape. But for small field intensity F, the escape rate is unmeasurably small. As the field increases, a point F^* is finally reached at which ionization rate rapidly enters the region of experimental observability. It is this point – the "critical ionization field" – which needs to be predicted, and has importance for analysis of highly excited Rydberg levels.[30]

This situation is analogous to that of cooling a vapor slowly below its thermodynamic condensation temperature T_b. For any temperature $T < T_b$ there is a positive nucleation rate for transition to liquid, but small undercooling can correspond to geologically long lifetimes of the metastable vapor. Only as a critical under-cooling limit is approached with the homogeneous nucleation rate suddenly rise to the point of observability in the usual laboratory time scale.[31] It is the task of nucleation theory to predict this point at which the metastable vapor undergoes catastrophic and sudden condensation.

Nonlinear variational calculations can serve a similar purpose for quantum mechanical problems for which catastrophic breakup of a bound system is involved (autoionization, rotational predissociation, field ionization, etc.). If a proper variational basis is used, the predicted energy $E_o(\lambda)$ will exhibit a branch point at a characteristic value of the perturbation strength, λ^*. As usual, the imaginary part of $E_o(\lambda)$ beyond the branch point represents a measurable lifetime for the complex. Energy (and orbital parameter) bifurcation produced by the nonlinear variational calculation is indicative of results that appear generally in "catastrophe theory".[32] Using a simple nonlinear variational wavefunction, for instance, Herrick[33] obtained analytic formulas for the critical ionization field for Rydberg levels of hydrogen in terms of the zero-field Stark quantum numbers. The important point is that the variational calculations can yield the critical field directly, without a supplementary computation of the ionization rate.

By analogy, the critical value $\lambda^* > \lambda_c$ predicted by calculations[16] for atomic isoelectronic series would also mark the onset of rapid ionization. A knowledge of λ^* for a particular system would therefore be useful for predicting the stability of a given doubly-charged anion.

Molecular Crossings

There is considerably more freedom for continuum crossings in molecules. Here λ might represent a scaled nuclear charge for either the entire molecule or perhaps just a portion of it. More important is the case where λ represents a continuous transformation of the $3N-6$ internal vibrational coordinates for an N-atom molecule. For diatomics the familiar "noncrossing rule" prevents two

Born-Oppenheimer potential energy curves of the same symmetry from intersecting. This rule does not prevent a level from entering a continuum of states. A frequently occurring system for a diatomic AB involves a repulsive energy curve which penetrates the ionization threshold for AB^+ at a finite internuclear separation R_c. The $(2p\sigma_u)^2\ ^1\Sigma_g^+$ state of H_2, for instance, crosses the $(1s\sigma_g)^2\ ^2\Sigma_g^+$ state of H_2^+ at $R_c = 1.5$ Å. Interactions with molecular Rydberg levels just below this threshold can lead to production of high Rydberg levels in the separated atoms.[34] This crossing is clearly "soft", owing to the Rydberg levels. An example of a "hard" adiabatic diatomic crossing is evident in the process

$$H^- + H^- \rightarrow H + H^- + e^-.$$

The ionization probability, $\Gamma(R)$, could be found by analytic continuation of the adiabatic bound state potential energy curve above threshold.

Continuum crossings for polyatomics are even more interesting, since the threshold may be crossed in any number of ways. For adiabatic energy surfaces, however, the same resonance energy and width should be obtained for a given molecular geometry, independently of the direction of approach from below threshold. The elementary models of "catastrophe theory",[32] together with nonlinear variation theory, offer the potential for a mathematical classification of the types of electronic breakup which can arise from large amplitude vibrationally-induced continuum crossings.

One case of recent interest[35] involves the potential energy surfaces for electron autodetachment from CO_2^-. In terms of the OCO bending angle α, the anion potential energy minimum lies below threshold at 135°. The anion is energetically less stable for higher angles and intersects the ionization threshold for $CO_2 + e^-$ near $\alpha = 150°$. Presumably there exists a resonance state for $\alpha > 150°$, having both a maximum energy and width in the linear geometry. If the continuum crossing indicated by the calculations is accurate (i.e., has a nonzero intersection slope), then more refined wavefunctions should yield a critical angle α^* above which the variational energy is complex. Bruna et al.[35] suggested that a low lying series of diffuse anion states may have greater importance to vertical autodetachment than does the valence state, which is thought to lie too high above threshold to explain experiment. However, it is possible that this series of states does not cross into the continuum but is tangent to it at some $\alpha \neq 180°$, on account of a long-range attraction between the electron and the dipolar bent CO_2. If the isoelectronic atomic calculations[16] are also typical of energy behaviour near α^*, then the outer orbital for CO_2^- should becomerapidly more diffuse as α nears α^*. This instability would shift the resonance energy downward for $\alpha > \alpha^*$. For instance, the predicted 0^{2-} resonance[17] energy was 0.7 eV lower than the SCF value, due to continuum interactions. Similar behavior may occur for molecular states, and should not be overlooked in computations. $A^2\Pi_n$ shape resonance is known to exist at 3.8 eV in the electron impact

spectrum of CO_2.[36]

Conclusion

The decay of a resonance state has traditionally been described in terms of a bound state wavefunction which interacts with an adjacent continuum. The theory of "bound states in the continuum" provides a means for constructing real, local potentials which can render the resonance state stable above threshhold. The difference between this model potential and the exact physical potential is the "perturbation" by which the bound state decays. Although little is known about rigorous bound states in the continuum for many-particle systems, investigations of continuum crossing phenomena in the light of current knowledge may offer insight to unexpected stability in systems which might otherwise be thought of as highly unstable.

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