Conical Intersections and Bound Molecular States Embedded in the Continuum

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Nuclear dynamics on coupled potential surfaces can lead to bound states embedded in the continuum. For one type of conical intersection situation, an explicit proof is presented that such states exist. Non-Born-Oppenheimer effects are responsible for the binding of these states. Once the Born-Oppenheimer approximation is introduced, these states at best become resonances which decay via potential tunneling. The tunneling is completely suppressed by the coupling between the electronic states. A numerical example is given.

In general, scattering cross sections exhibit local extrema which are attributed to compound states of the target plus projectile system. These states, often called resonances, are nonstationary states of finite lifetime and can be described as discrete states embedded in and interacting with the continuum [1]. Two questions immediately arise. Can this interaction with the continuum be totally suppressed and if yes, why? The absence of interaction leads to *bound states* with energies embedded in the continuous spectrum. Such states were first discussed by von Neumann and Wigner in 1929 [2]. They proposed that certain spatially oscillating potentials, with amplitude decreasing with distance, could support bound states at positive energies. At specific momenta destructive interference occurs, which causes the wave function to vanish at large distances producing thereby a normalizable state.

The results of von Neumann and Wigner have stimulated a considerable amount of theoretical and also experimental work of which we cite only a few. One example is provided by Capasso *et al.* [3] who report on an electronic bound state with no classical turning points which they have observed in a superlattice consisting of ultrathin semiconductor layers. Another example is given by Weber and Pursey [4] who discuss truncated von Neumann—Wigner potentials in connection with the reported observations of narrow positron-electron peaks in heavy ion collisions [5] which could be fingerprints of the existence of bound states in the continuum.

The von Neumann–Wigner potential is a long-range potential and its truncation turns the bound state into a resonance state [4]. In the present work we demonstrate that there exists another class of physical problems with bound states in the continuum where no use is made of the long-range property of the underlying potentials.

Moreover, the physical problems are realized in real systems.

In molecules the fundamental Born-Oppenheimer approximation [6], which separates the electronic and the nuclear motions, is often valid. There are, however, numerous examples where this approximation becomes inadequate or even breaks down. In these cases two (or more) electronic states interact with each other through the nuclear motion. The generic prototype situation where the Born-Oppenheimer approximation breaks down is provided by the presence of conical intersections of electronic energies in the space of nuclear coordinates [7]. These energies are the potential surfaces for the nuclear motion. Conical intersections [8] of potential surfaces are in fact ubiquitous [7,9–11]. They have been abundantly found in triatomic molecules as well as in large polyatomic ones. In this work we demonstrate that conical intersection situations provide a mechanism for bound states embedded in the continuum.

We consider the nuclear motion on two coupled potential surfaces. A diabatic representation [12] of the electronic states is invoked which, although not strictly existent [13], provides a widely used framework for understanding the dynamics in conical intersection situations of real molecules. The proof of the existence of bound states in the continuum is presented below in the diabatic representation for simplicity of representation; it can also be given invoking the adiabatic representation. The Hamiltonian in matrix notation reads

$$\mathbf{H} = T_N \mathbf{1} + \begin{pmatrix} V_b & V_{bc} \\ V_{bc} & V_c \end{pmatrix}, \qquad (1)$$

where T_N is the kinetic energy operator of the nuclei and $\mathbf{1}$ denotes a two dimensional unit matrix. V_b and V_c are the

diabatic potential surfaces of the two electronic states which are coupled via the potential coupling V_{bc}. In general, all these potentials are functions of the participating nuclear coordinates. Symmetry, however, plays an essential role in shaping these potentials.

A widespread type of conical intersection arises from two nondegenerate electronic states Φ_b and Φ_c of different spatial symmetries [7]. The case of states of the same symmetry is more involved and is not discussed here. Let us denote the two symmetries by B and C, their product by D, $D = B \times C$, and the totally symmetric symmetry representation of the underlying Abelian point group by A. The nuclear coordinates (modes) relevant for the dynamics can be easily identified by symmetry. The two electronic states interact through those nontotally symmetric nuclear modes which transform as D, while the totally symmetric modes regulate the separation in energy of the interacting states [7]. Let us denote the former modes by y, the latter by x, and all other types by z and consider for simplicity of the discussion one mode of each type. The full Hamiltonian H and the kinetic energy operator T_N are totally symmetric. Consequently $V_b = \langle \Phi_b | H - T_N | \Phi_b \rangle$ and similarly V_c in (1) are totally symmetric functions of the nuclear coordinates, i.e., $V_b = V_b(x, y^2, z^2)$ and $V_c = V_c(x, y^2, z^2)$. These can be expanded in a Taylor series in the vicinity of a relevant reference point, e.g., the ground state geometry: $V_b = V_b(0) + k_b x + O(2)$ and $V_c = V_c(0) + k_c x + O(2)$, where the ks are the gradients of the potentials with respect to x and $O(2)$ refers to all second order distortions. In contrast, $V_{bc} = \langle \Phi_b | H - T_N | \Phi_c \rangle$ obviously transforms as D and is an odd function in y. We may write $V_{bc} = y\lambda(x, z^2, y^2) = y\lambda(0) + O(2)$. We see that the totally symmetric modes x enter the diagonal in (1) linearly while the nontotally symmetric modes y influence linearly the off diagonal. For further discussion of symmetry, see, for instance, [14].

At a conical intersection the adiabatic potential surfaces intersect linearly in at least two nuclear coordinates. Clearly these coordinates comprise at least one coupling mode y and one totally symmetric mode x. The modes of type z are irrelevant in the vicinity of the conical intersections. The adiabatic potential surfaces are obtained as the eigenvalues of the potential matrix in (1). For these eigenvalues to coincide, the conditions $V_b = V_c$ and $V_{bc} = 0$ must be fulfilled. The above symmetry considerations imply that a conical intersection exists at $y = 0$ and $x = [V_b(0) - V_c(0)]/[k_c - k_b] + \ldots$ if the gradients differ from each other and the Taylor series of the diabatic potentials still hold at this geometry. Nowadays, *ab initio* methods are available to detect conical intersections [10] and once such an intersection is found we can choose the geometry of this intersection as our reference point for the above symmetry considerations.

Having completed the discussion of symmetry in the basic equation (1), we now return to our main topic of bound states in the continuum and consider the electronic state Φ_b to be bound in all nuclear modes (up to some energy of interest) while the other electronic state Φ_c is dissociative in one direction and bound in the others. For simplicity, one coupling mode y and one totally symmetric mode x are considered and the dissociation is along the mode x. The analysis presented below can be straightforwardly transferred to other situations. Conical intersections involving dissociative and bound electronic states are widespread and play an important role in, e.g., photodissociation processes; see [9–11,15,16] and references therein.

To proceed we introduce the Hamiltonians $H_b = T_N + V_b$ and $H_c = T_N + V_c$ which describe the nuclear motion in the uncoupled electronic states. Of course we are interested in the Schrödinger equation of the total Hamiltonian (1):

$$\begin{pmatrix} H_b & V_{bc} \\ V_{bc} & H_c \end{pmatrix} \begin{pmatrix} \psi_b \\ \psi_c \end{pmatrix} = E \begin{pmatrix} \psi_b \\ \psi_c \end{pmatrix}, \qquad (2)$$

where ψ_b and ψ_c are the components of the nuclear wave function on the two diabatic surfaces. The states of H_c provide the continuum for the bound vibrational states of H_b which become, in general, resonances through the coupling V_{bc}. At large values of x the modes x and y become separable in H_c and at $x \rightarrow \infty$ we have $H_c = T_x + [T_y + V_c(y)]$ which will be denoted $H_c(\infty)$ in the following. T_x and T_y are the kinetic energy operators of the x and y motions and $V_c(y)$ collects all the constants and y-dependent potential contributions. Let us denote the eigenenergies of $T_y + V_c(y)$ by E_{m_y} and its eigenstates by $|m_y\rangle$; $m = 0, 1, \ldots$. The energies of the various channels to which the system can dissociate are E_{m_y} and the threshold of the dissociation is obviously given by the lowest of these values, E_{0_y}, i.e., by the ground state energy of $H_c(\infty)$.

Upon expanding (2) into two equations, solving for ψ_c in one equation in terms of ψ_b while adding the infinitesimal $i0^+$ to the resolvent, and substituting the resulting equation for ψ_c into the other equation, we obtain

$$H_R \psi_b = E \psi_b, \qquad (3)$$

where H_R is the effective, energy-dependent Hamiltonian describing the states of H in the bound subspace of H_b:

$$H_R = H_b + V_{bc}(E - H_c + i0^+)^{-1} V_{bc}. \qquad (4)$$

The solutions of (3) in the complex energy plane provide the bound and resonance states of H.

Since H_R lives in the bound space of H_b, ψ_b is a square integrable function and we may normalize it. In general, the complex resonance energy E is given as $\langle \psi_b | H_R | \psi_b \rangle$:

$$E = \langle \psi_b | H_b | \psi_b \rangle + \langle \psi_b | V_{bc}(E - H_c + i0^+)^{-1} V_{bc} | \psi_b \rangle. \qquad (5)$$

The first term on the right-hand side is a real number, and

the second term can take on complex values. Since the resolvent $(E - H_c + i0^+)^{-1}$ possesses a cut at energies at and above the continuous spectrum of H_c, one might be tempted to assume that all levels at energies above the dissociation threshold of H_c are resonances. This is, however, incorrect as we show below.

To evaluate (3), we may represent H_R in (4) in the complete discrete product basis (H_R lives in the bound subspace of H_b) $|n_x\rangle|m_y\rangle$, where the $|m_y\rangle$ have been introduced in the text below (2) and the $|n_x\rangle$ are ordinary harmonic oscillator states. Because of symmetry, H_R does not couple even and odd values of m_y and we may investigate each set separately. For brevity we discuss only symmetric (gerade) states of y. We proceed by inserting into (4) the completeness relation of the set $|k_x\rangle|m_y\rangle$, where $|k_x\rangle$ are the free states of the kinetic energy operator T_x. The quantity $|k_x\rangle|m_y\rangle$ is an eigenstate of $H_c(\infty)$. The energies of the latter determine the cuts of H_R and hence the appearance of imaginary contributions to the resonances. We have argued above that H_c is a totally symmetric operator and the coupling potential V_{bc} an odd function of the coupling mode y. Consequently, the gerade states of H_R couple to the continuum via ungerade states of H_c as can be seen in (4).

Although the continuous spectrum of H_c begins at the breakup threshold E_{0_y}, the effective threshold for the gerade states of the total Hamiltonian is determined by the ungerade channel $|1_y\rangle$,]; i.e., it is at E_{1_y}. There are no gerade resonances of H at energies below E_{1_y}. The gerade states of H_R at these energies are true bound states embedded in the continuum. The latter begins at E_{0_y}. This completes our rigorous proof that conical intersections of the type discussed here give rise to bound states in the continuum.

In the following we briefly discuss a numerical example illuminating the above findings. To make the discussion as transparent as possible a simple structure for the diabatic potentials is chosen:

$$V_b = \tfrac{1}{2}\omega_x x^2 + \tfrac{1}{2}\omega_y y^2,$$
$$V_c = \epsilon e^{-\beta(x+\delta)} + \tfrac{1}{2}\omega_y y^2 + \Delta, \qquad V_{bc} = \lambda y. \qquad (6)$$

The bound Hamiltonian H_b is a separable sum of harmonic oscillators and the unbound part of V_c is an exponential function along the mode x. The coupling V_{bc} is linear in the coupling mode y as in previous models [7]. Dimensionless coordinates and atomic units are used. We have chosen values of the potential parameters to be $\omega_x = 0.015$, $\omega_y = 0.009$, $\epsilon = 0.04$, $\beta = 0.5$, $\delta = 0.5$, $\Delta = 0$, and $\lambda = 0.01$. A cut of the potentials along x at $y = 0$ is shown in Fig. 1. The two potentials V_b and V_c intersect at one point which turns out to be the conical intersection point of the adiabatic potential surfaces.

We have computed the eigenstates of the Hamiltonian (1) describing the nuclear dynamics on the coupled electronic states using the model potentials (6). For this
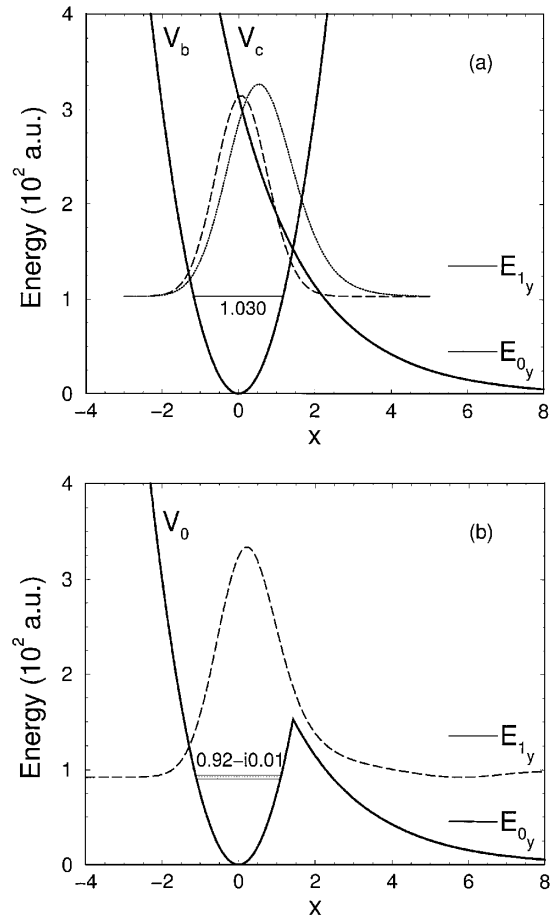

FIG. 1. (a) A cut of the diabatic potentials V_b and V_c along x at $y = 0$. Shown also are the exact energy of the bound state in the continuum and its wave function components $|\psi_b|^2$ (dashed curve) and $|\psi_c|^2$ (dotted curve); the latter has been scaled by a factor of 10 relative to the former. Both components exponentially decay at large x. The energy window for bound states in the continuum is indicated: it is between the breakup channels E_{0_y} and E_{1_y}. (b) A cut of the lower adiabatic potential along x at $y = 0$. The resonance state shown possesses a short lifetime due to tunneling; the resonance wave function oscillates at large x. The complex resonance energy is indicated; the horizontal thin dotted line indicates the resonance position and the horizontal thin solid lines indicate the width. Tunneling is completely suppressed by non-Born-Oppenheimer effects as seen in (a). The values of the potential parameters used are given in the text below Eq. (6). All of the wave functions are shown along x at $y = 1.2$ since ψ_c has a node at $y = 0$. Except for ψ_c, the wave functions shown are very similar in form to those for $y = 0$.

purpose the method of complex rotation [17] has been employed in which the Hamiltonian is analytically continued and the spectrum rotates into the complex energy plane. Bound state energies of the original Hamiltonian stay on the real energy axis while resonance states appear as isolated poles at complex energies $E_\alpha - i\Gamma_\alpha/2$. The width Γ_α of the resonance is inversely proportional to its lifetime. The resonance wave function of the complex

rotated Hamiltonian is an L^2 function in coordinate space underlying the conceptual and technical advantages of the approach. We did not *a priori* assume that the state of interest is a bound state. We rather computed it as a resonance and made sure that its width approaches zero as the number of basis functions used is systematically increased. For the parameters used in Fig. 1 we find a level at $E_\alpha = 0.010\,30$ with an imaginary part which is vanishingly small within numerical accuracy. This level is below E_{1_y} and above E_{0_y} as indicated in the figure. The wave function of this bound state embedded in the continuum is depicted in the figure as well. Although V_c is unbound, *both* components ψ_b and ψ_c of the total wave function [see (2)] are well localized in space as expected for a true bound state. We point out that resonances in potentials like those shown in Fig. 1 have been studied in real molecules and all previous examples have been found to have finite lifetime [18].

The coupling of electronic states leads to violations of the Born-Oppenheimer approximation. The question immediately arises whether the bound states found above are fingerprints of such violations or whether these states also exist within the Born-Oppenheimer approximation. In this approximation the nuclear dynamics proceeds on the uncoupled adiabatic potential surfaces using the kinetic energy operator T_N. The adiabatic surfaces are obtained as eigenvalues of the potential matrix in (1). A cut of the lower adiabatic potential along x at $y = 0$ is shown in Fig. 1 for the potentials in (6). We have computed the resonance state in the adiabatic potential and obtained $E_\alpha^{(\mathrm{ad})} = 0.0092 - i0.0001$. Obviously the width of this state is substantial although the real part of the energy resembles the exact solution of the Schrödinger equation (2). This width is a result of tunneling through the potential barrier. In the exact calculations, this tunneling is completely suppressed by the coupling between the electronic states.

Summarizing, we have demonstrated that the nuclear dynamics on coupled potential surfaces possess attractive features which can lead to bound states embedded in the continuum. In the conical intersection situation studied here a rigorous proof is given that an energy window in the continuum exists whose gerade states are bound. The binding is absent in the widely used Born-Oppenheimer approximation where the dynamics proceeds on a single adiabatic surface at a time and the standard kinetic energy is used. It would be interesting to study the impact of corrections to this approximation by introducing a geometic phase [19]. (Note that the geometric phase effect is included in our above calculations of bound states embedded in the continuum.) Bound states in the continuum cannot be observed in scattering experiments but can be observed by spectroscopy and half-collision experiments. If the system is perturbed and its symmetry lowered, the bound states in the continuum will turn into resonances

which, most probably, are very long-lived. The appearance of sharp peaks in scattering cross sections in conical intersection situations of the type discussed here is an indication of these resonances and hence of the mechanism discussed here. It could be the case that other types of interactions betweeen electronic states also lead to bound states, but we are not presently aware of such cases.

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