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Feshbach Resonances: The Branching of Quantum Mechanics into Hermitian and Non-Hermitian Formalisms[†]

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As has been shown long time ago by Feshbach, the *exact* energy spectrum of the full problem can be obtained by solving two different self-energy problems. In spite of the fact that the two effective Hamiltonians are derived in very similar ways in one case, the exact energy spectrum of the full problem can be either real or complex (depending on the boundary conditions), whereas the exact energy spectrum associated with the second effective Hamiltonian has to be complex (excluding bound states in the continuum). The focus of this paper is on the fact that in both cases the complex eigenvalues result from the *same* requirement of an outgoing boundary condition. The branching of quantum mechanics to standard (Hermitian) formalism and non-Hermitian formalism is associated with the decision to express the exact energy spectrum with one of the two possible self-consistent like problems where the use of the Green operator imposes an outgoing boundary condition on the solutions of the time-independent Schrödinger equation. Our analysis is made for the case where an ABC molecule has sufficient energy to dissociate to A + BC but not to A + B + C and not to AB + C or to AC + B.

A fundamental postulate in the standard quantum mechanics is that any measurable dynamical quantity is presented by a Hermitian operator. This postulate results from another postulate in quantum mechanics which states that any quantities that will ever be observed are the eigenvalues of operators that represent the measurable quantities. Since the measurable quantities such as velocity of free particles or energy of stable atoms and molecules are real quantities, the operators that represent the velocity or the total energy or any other quantity of bound systems should be Hermitian operators. However, these operators $\hat{O}$, which represent measurable dynamical quantities, are Hermitian provided they operate on functions from a Hilbert space $\mathscr{H}$ such that $\langle f|\hat{H}|g\rangle = [\langle g|\hat{H}|f\rangle]^*$, where f and g are square integrable functions, $f, g \in L_2(\mathbb{R}) = \mathscr{H}$, or periodic functions. The consequences of this postulate are a series of theorems that serve as milestones in the formalism of quantum mechanics. The eigenvalues of the Hermitian operators are real and expectation values of any measurable quantity are real. The eigenfunctions of the Hermitian operators can serve as a complete set in the series expansion of any wavepacket (including time-dependent wavepackets) that represent the system under study. That is, $|\Psi\rangle = \sum_j c_j|j\rangle$, where $\hat{O}|j\rangle = o_j|j\rangle$. The absolute value of any one of the expansion coefficients, $|c_j|^2$, is the probability of measuring a specific quantity, o_j. This formalism does not hold when quantum mechanics is derived within the framework of the non-Hermitian approach. Within the framework of the non-Hermitian formalism of quantum mechanics, outgoing boundary conditions are imposed on the eigenfunctions of the Hamiltonian. In the case of bound states, the same solutions as in the standard (Hermitian) formalism are obtained since the asymptotes of bound states are out going waves with purely imaginary positive wave vectors. However, by imposing outgoing boundary conditions on the continuum eigenfunctions (i.e., the amplitudes of the incoming waves are equal to zero as in the case of bound states), complex eigenvalues are obtained associated with eigenfunctions that exponentially diverge and by definition are not embedded in the Hilbert space. Therefore, the Hamiltonian becomes non-Hermitian due to the fact that the eigenfunctions are not in the Hilbert space as required within the framework of the standard (Hermitian) formalism of quantum mechanics.[1] These special solutions are associated with the complex poles of the scattering matrix that are obtained within the framework of the standard formalism of quantum mechanics.[2] These poles are known as resonance states and describe metastable states of the studied system that as time passes breaks into subsystem. When the subsystems are ion and electrons, this is either an autoionization[3] or Auger ionization[4] or intra-Coulombic decay (ICD) resonance phenomenon.[5] When the subsystems are molecular radicals, atoms, or molecules, this is the predissociation resonance phenomena.[6] It is a point of interest to mention here that by applying complex scaling transformations these resonance states decay exponentially and become square integrable functions that are embedded in the general Hilbert space (see reviews in refs 2 and 7). In this paper, we will not consider the complex scaling transformation and will focus on the association of the predissociation resonances with the solutions obtained by applying the Feshbach formalism to the closed channels and not to the open ones as usually it is done in molecular physics studies. The idea to apply the Feshbach formalism to the closed channels is not new and has been done before by Feshbach for nuclear physics problems.[8] Here we apply this approach to molecular physics problems, emphasizing the role of the Green function in imposing outgoing boundary conditions on the solutions which are associated with the open channels and emphasizing the fact that by doing so we get into the non-Hermitian sector of the domain of the

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Hamiltonian. We also emphasize in our derivation and discussions presented here the branching of quantum mechanics into the Hermitian and non-Hermitian formalisms when the Feshbach effective Hamiltonians are derived. We stress the fact that complex eigenvalues are obtained not only by solving the time-independent Schrödinger equation for the closed channel's Feshbach effective Hamiltonian but also for the full physical Hamiltonian when outgoing boundary conditions are imposed on the solutions that are embedded in the continuum part of the spectrum.

In contrast to Hermitian Hamiltonians, which always have a diagonalizable spectral decomposition in eigenfunctions, non-Hermitian Hamiltonians may contain nondiagonalizable (Jordan) blocks in their spectral decomposition consisting of eigenfunctions (so-called incomplete spectrum, where the number of the linearly independent eigenvectors of a given square matrix that represents the operator is smaller than the dimension of the matrix) and so-called associated functions (see refs 9−11, where it has been proved that a non-Hermitian Hamiltonian which consists of a linear combination of two Hermitian noncommutative operators always can have an incomplete spectrum). This structure, which superficially might lead to the formal impression of an incompleteness of the basis set and a defect in the eigenvalues, merely indicates the appearance of new effects compared to those known for standard Hermitian Hamiltonians. Another difference between the standard formalism of quantum mechanics and the non-Hermitian formalism is that the eigenvalues associated with measurable quantities and expectation values can get complex values. However, for this price, which is not as great as one might expect, we gain by having a formalism that simplifies the analytical and numerical calculations of a large number of quantities of very different types that are associated with the resonance phenomena.

In spite of the requirement of the physical operators to be Hermitian, non-Hermitian Hamiltonians appear in the standard (conventional) quantum mechanics formalism when effective Hamiltonians are derived. Let us briefly describe how they are obtained and what are the significant results of that derivation and its relevance to very general physical phenomena known as Feshbach resonances for a multidimensional system.[8,12,13]

In this paper, we will focus on the Feshbach resonances of a three-atom molecule ABC when the following chemical reaction takes place: ABC→A + BC. The Hermitian Hamiltonian of the system under our study, $\hat{H}$, is a three-atom molecule ABC, which depends on two types of coordinates **r** associated with the diatom BC and R associated with the position of the atom A with respect to the center of mass of the diatom such that

$$\hat{H} \rightarrow \hat{T}_R + \hat{H}_{\text{final}}(\mathbf{r}) \tag{1}$$

as

$$R \rightarrow \infty \tag{2}$$

where $\hat{H}_{\text{final}}(\mathbf{r}) = \hat{T}_{\mathbf{r}} + \lim_{R\to\infty} V(\mathbf{r},R)$, and $\hat{T}_R$ and $\hat{T}_{\mathbf{r}}$ are the kinetic operators associated respectively with the "dissociative" coordinate R that indicates the position of atom A with respect to the center of mass of the diatom BC, while the internal coordinate **r** indicates the position of B about C. The Hamiltonian that describes atom A and molecule BC obtained by the dissociation of ABC is $\hat{H}_{\text{final}}$. Since we assume here that the ABC molecule does not have enough energy to break the chemical bond BC, $\hat{H}_{\text{final}}$ has a discrete spectrum associated with the vibrational and rotational bound states of the diatom BC such that

$$\hat{H}_{\text{final}}(\mathbf{r})\chi_n(\mathbf{r}) = E_n^{\text{th}}\chi_n(\mathbf{r}) \tag{3}$$

where $n = 0,\ 1,\ 2, ...$ and $E_0^{\text{th}} < E_1^{\text{th}} \leq < E_2^{\text{th}} \leq ...$ and the corresponding eigenfunctions are bound states. The superscript th means that these bound states of the subsystem are the threshold energies in the spectrum of the full Hamiltonian. For example, in the case of three-atom molecule ABC, where the final state consists of an atom A and diatom BC (there is no interaction between A and BC), the bound state energies of the diatomic molecule BC are the threshold energies of the full three-body system ABC. For diatoms $n = 0,\ 1,\ 2, ...$ is a superindex that stands for two good quantum numbers that are associated with the rotational and the vibrational motions.

As mentioned above, we do not consider here the situation where the system falls completely apart and the final Hamiltonian is associated with three atoms A + B + C, which are moving freely without interacting among themselves.

The atom A is temporarily trapped by the diatom BC, due to the potential of interaction $V(\mathbf{r}, R)$, where R is the distance of atom A from the center of mass of BC. **r** represents the internal coordinates of the diatom. The time-independent Schrödinger equation we solve here is given by

$$\hat{H}\Psi(R, \mathbf{r}) = E\Psi(R, \mathbf{r}) \tag{4}$$

where E is in the continuum part of the spectrum of $\hat{H}$. We can expand the eigenfunction $\Psi(R, \mathbf{r})$ by using the eigenfunctions of $\hat{H}_{\text{final}}$ as a basis set

$$\Psi(R, \mathbf{r}) = \sum_n \phi_n(R)\,\chi_n(\mathbf{r}) \tag{5}$$

Note that, in order to simplify the notation, we do not label $\Psi(R, \mathbf{r})$ by an index that is associated with the energy E. On purpose we do not label $\Psi(R, \mathbf{r})$ by another index that labels the entrance channel in the scattering process, since unlike the standard (Hermitian) formalism of quantum mechanics, where the amplitude of the incoming wave gets a finite nonvanishing values, within the framework of the non-Hermitian formalism of quantum mechanics we impose on the amplitude of the incoming wave to be vanished. We can split this summation into two parts based on the fact that $n > n_c$ are closed channels for "dissociation", since $E < E^{\text{th}}_{n>n_c}$, whereas $n \leq n_c$ are open channels for "dissociation", since $E > E^{\text{th}}_{n\leq n_c}$. Following the Feshbach formalism, $\{Q\}$ denotes the subspace of the closed channels, and $\{P\}$ of the open channel subspace. Therefore, $\{Q\} \cong \{\chi_{n>n_c}\}$, and $\{P\} \cong \{\chi_{n\leq n_c}\}$. Using $\chi_n(\mathbf{r})$, which are associated with the closed and the open channels as a basis set, eq 4 can be represented in the following matrix form

$$\begin{pmatrix} \mathbf{H}_{QQ} & \mathbf{H}_{QP} \\ \mathbf{H}_{PQ} & \mathbf{H}_{PP} \end{pmatrix} \begin{pmatrix} \vec{\phi}^{Q}(R) \\ \vec{\phi}^{P}(R) \end{pmatrix} = E \begin{pmatrix} \vec{\phi}^{Q}(R) \\ \vec{\phi}^{P}(R) \end{pmatrix} \tag{6}$$

where

$$\begin{aligned}
[\mathbf{H}_{QQ}]_{n',n} &= \langle \chi_{n'>n_c}|\hat{H}|\chi_{n>n_c}\rangle_{\mathbf{r}} \\
[\mathbf{H}_{PP}]_{n',n} &= \langle \chi_{n'\le n_c}|\hat{H}|\chi_{n\le n_c}\rangle_{\mathbf{r}} \\
[\mathbf{H}_{QP}]_{n',n} &= \langle \chi_{n'>n_c}|\hat{H}|\chi_{n\le n_c}\rangle_{\mathbf{r}} \\
[\mathbf{H}_{PQ}]_{n',n} &= [\mathbf{H}_{QP}]^*_{n,n'}
\end{aligned} \tag{7}$$

and

$$\begin{aligned}
[\vec{\phi}^Q(R)]_n &= \phi_{n>n_c}(R) \\
[\vec{\phi}^P(R)]_n &= \phi_{n\le n_c}(R)
\end{aligned} \tag{8}$$

The subscript **r** introduces an integral over this variable only.

The system as defined by the Hamiltonian in eq 6 may be reduced to two types of effective theories. One only in terms of the ϕ^P components when we eliminate from the problem the *closed* channels, while in the other approach, an effective theory is derived in terms of the ϕ^Q components, eliminating from the problem the *open* channels. *In both cases the elimination of the closed or the open channels from the problem is not an approximation and in both cases the exact energy spectrum of the problem is obtained.* In our discussion given below, we emphasize the association of the standard formulation of quantum mechanics with the decision to derive the effective theory in one way while the decision to derive an effective theory by the other approach leads to the formulation of a non-Hermitian quantum mechanics where metastable-resonance states are associated with complex eigenvalues of the time-independent Schrödinger equation as given in eq 4.

The two coupled equations presented in eq 6 can be reduced to the following self-consistent like eigenvalue problem

$$[\mathbf{H}_{PP} + \mathbf{H}_{PQ}\mathbf{G}^+_{QQ}(E)\mathbf{H}_{QP})\vec{\phi}^P(R) = E\vec{\phi}^P(R) \tag{9}$$

where

$$\mathbf{G}^+_{QQ}(E) = \lim_{\epsilon\to 0+}(E\mathbf{I} - \mathbf{H}_{QQ} + \mathrm{i}\epsilon) \tag{10}$$

In the transition from eq 6 to eq 9, we expressed $\vec{\phi}^Q$ in terms of $\vec{\phi}^P$

$$\vec{\phi}^Q = \vec{\varphi}^Q + \mathbf{G}^+_{QQ}(E)\mathbf{H}_{QP}\vec{\phi}^P \tag{11}$$

where $\vec{\varphi}^Q$ is the homogeneous solution such that

$$(E\mathbf{I} - \mathbf{H}_{QQ})\vec{\varphi}^Q = 0 \tag{12}$$

Since E is a continuous variable while the spectrum of $\mathbf{H}_{QQ}$ is discrete, we have chosen as the homogeneous solution $\vec{\varphi}^Q = 0$. Note that $\vec{\phi}^Q$ is a square integrable function, which implies that $\vec{\phi}^Q$ has outgoing boundary condition with purely imaginary momentum, and consequently, by taking the homogeneous solution as zero, we do not change the boundary condition of $\vec{\phi}^Q$. The term $+\mathrm{i}\epsilon$ in the Green operator ensures that in eq 11 only outgoing waves will be present in the closed channels $\vec{\phi}^Q$ [see eq 8 for the definition of the closed and open channels]. The requirement on $\vec{\phi}^Q$ to have outgoing wave asymptotes does not cause any problem, since the asymptotes of bound states are indeed outgoing waves, exp(ikR) with $\mathscr{R}k = 0$ and $\mathscr{I}k > 0$.

The self-energy Hamiltonian given in eq 9 contains a nonlocal, energy-dependent, and *non-Hermitian* operator, which is known as the *optical potential*[15]

$$\mathbf{V}^P_{\mathrm{opt}}(\mathbf{R}, E) = \mathbf{H}_{PQ}\mathbf{G}^+_{QQ}(E)\mathbf{H}_{QP} \tag{13}$$

The physical meaning of the optical potential is clarified by replacing the full Hamiltonian by an effective Hamiltonian for the open channels only. The optical potential introduces processes in which particles in the closed channels, $\vec{\phi}^Q$, are scattered into one or into several open channels.

Our proposition for a simple "point" where QM branches into the standard (Hermitian) formalism and the non-Hermitian formalism is based on the fact that the term iϵ in the Green operator, $\hat{G}^+(E) = \lim_{\epsilon\to 0+}(E + \mathrm{i}\epsilon - \hat{H})^{-1}$ introduces outgoing wave boundary conditions on $|F\rangle = \hat{G}^+(E)|f\rangle$ for any wavepacket $|f\rangle$ that can be described as a linear combination of incoming and outgoing waves. Although this fact is known (see, for example, ref 16), for the sake of coherency of our presentation, we briefly explain it in the Appendix.

Let us now return to the self-energy problem, eq 9. This equation can be solved by an iterative procedure where in every step of the iteration an eigenvalue problem is solved for a non-Hermitian Hamiltonian. Since the original Hamiltonian $\hat{H}$ is an Hermitian operator, the energy E gets real values only. Therefore,

$$\hat{H}^P_{\mathrm{eff}}(E)\,\vec{\phi}^P(R) = E\vec{\phi}^P(R) \tag{14}$$

where E is real, although the *effective* Hamiltonian is non-Hermitian,

$$\hat{H}^P_{\mathrm{eff}} = \mathbf{H}_{PP} + \mathbf{V}^P_{\mathrm{opt}}(R, E) \tag{15}$$

Since in the Hermitian (standard) formalism of quantum mechanics the amplitude of the incoming waves get nonzero values, the spectrum of $\hat{H}^P_{\mathrm{eff}}$ is real as the spectrum of the full Hamiltonian. The key point in this derivation is in the fact that within the framework of the Feshbach formalism[13] the non-Hermitian optical potential has been derived for the open channel, where the $+\mathrm{i}\epsilon$ in the denominator of the Green operator, as defined in eq 10, imposes outgoing boundary conditions on the $\vec{\phi}^Q$, which are associated with the closed channel. As it has already been mentioned above, the requirement of outgoing wave boundary conditions from bound states does not produce a flux, since $\lim_{R\to\infty}\phi^Q(\mathrm{R}) = \mathbf{A}\exp(\mathrm{ikR}) \to 0$, where $\mathscr{R}\mathrm{k} = 0$ and $\mathscr{I}k > 0$. What about the asymptotes of the open channels? In order to get stationary solutions (i.e., flux is conserved), the asymptotes of the open channels should be scattering states

$$\phi_{n>n_c}(R) \to \sqrt{\frac{M}{\hbar k_n}}\exp(-\mathrm{i}k_nR) - \sum_{n'>n_c} S_{n,n'}(E)\sqrt{\frac{M}{\hbar k_{n'}}}\exp(+\mathrm{i}k_{n'}R) \tag{16}$$

where for $m > n_c$ (m stands for n or for n')

$$\frac{(\hbar k_m)^2}{2M} = E - E_m^{\mathrm{th}} \tag{17}$$

We can summarize the Feshbach formalism by saying that the derivation of the self-energy effective Hamiltonian eliminated the closed channels from the problem. The price we payed for it is the need to solve a noneigenvalue problem for a non-Hermitian, energy-dependent, and nonlocal Hamiltonian. However, since the boundary wave conditions are kept as in the original problem, i.e., square integrable bound states are associated with the closed channels and scattering states are associated with the open channels, the real energy E and the eigenfunctions of the full Hermitian Hamiltonian are obtained.[13] However, by imposing outgoing boundary condition on the solutions of eq 14, the amplitudes of the incoming wave are vanished, and consequently, the scattering matrix gets infinitely large values (i.e., $S_{n,n'}(E) = \infty$) when E get complex values. These complex values of E are the poles of the scattering matrix as obtained by solving the same equation, eq 14, within the framework of the standard formalism of quantum mechanics.

Let us briefly review here how the resonances that are associated with the poles of the **S**-matrix, i.e., $S_{n,n'}(E_{\mathrm{res}}) = \infty$, where $E_{\mathrm{res}} = E_{\mathrm{r}}(\text{energy} - \text{position}) - \mathrm{i}/2\Gamma(\text{width})$ were obtained in a very simple way as described a long time ago by Feshbach.[8] Here we will emphasize the outgoing boundary condition as described above, which are imposed by the Green function.

Instead of deriving the effective Hamiltonian for the open channels as described above and as appear in ref 13, the effective Hamiltonian as defined for the closed channels (ϕ^Q representation) will be derived (see ref 8). As we will show below, this is a very crucial point in our explanation of why complex energies are obtained by solving the self-consistent-like problem for the effective Hamiltonian as defined for the closed channels: The self-consistent-like problem for the effective Hamiltonian for the closed channels is given by

$$\hat{H}^Q_{\mathrm{eff}}(E)\,\vec{\phi}^Q(\mathbf{R}) = E\vec{\phi}^Q(R) \tag{18}$$

where

$$\hat{H}^Q_{\mathrm{eff}} = \mathbf{H}_{QQ} + \mathbf{V}^Q_{\mathrm{opt}}(R, E) \tag{19}$$

and the nonlocal energy operator that is associated with the effective Hamiltonian of the closed channels is defined as

$$\mathbf{V}^Q_{\mathrm{opt}}(\mathrm{R}, E) = \mathbf{H}_{QP}\mathbf{G}^+_{PP}(E)\mathbf{H}_{PQ} \tag{20}$$

where the Green operator is now associated with the open channel's Hamiltonian and *not* with the closed channel's Hamiltonian

$$\mathbf{G}^+_{PP}(E) = \lim_{\epsilon \to 0+} (E\mathbf{I} - \mathbf{H}_{PP} + \mathrm{i}\epsilon) \tag{21}$$

Here we are coming to a delicate point in our derivation. In the transformation of the original full problem as presented in eq 4 into eq 18 we used the following equality

$$\vec{\phi}^P = \mathbf{G}^+_{PP}(E)\mathbf{H}_{PQ}\vec{\phi}^Q \tag{22}$$

As explained in the Appendix, the term $+\mathrm{i}\epsilon$ as it appears in eq 21 ensures that the continuum functions $\vec{\phi}^P(E)$ as defined in eq 22 have outgoing waves only and therefore are associated with complex eigenvalues E. The only case where this kind of solution is obtained within the framework of the standard(hermitian) formalism of quantum mechanics is when there are true bound states in the continuum and E gets real values only.[14]

The requirement from $\vec{\phi}^P$ to have outgoing wave asymptotes implies that the amplitudes of the incoming waves vanish, and therefore, $S_{n,n'}(E) = \infty$ (see eq 16). The scattering state conditions that are needed to conserve the flux (see eq 16) are not satisfied. Imposing outgoing wave boundary conditions on $\vec{\phi}^P(\mathbf{R})$ imply that the flux is not conserved anymore. Therefore, when we disregard the possibility of bound states in the continuum,[14] $S_{n,n'}(E) = \infty$ for a *complex* value of $E = E_{\mathrm{res}}$, where $\mathscr{R}E_{\mathrm{res}}$ is in the continuum part of the spectrum. Since E for which eq 18 is satisfied is the eigenvalue of the original full problem, eq 4, it implies that $E = E_{\mathrm{res}} = E_{\mathrm{r}}(\text{position}) - \mathrm{i}/2\Gamma(\text{width})$ is a resonance solution of our problem. We should reemphasize the fact that the complex resonance eigenvalue $E = E_{\mathrm{res}}$ is obtained here by solving eq 18, where the complex resonance eigenvalue is associated with an eigenfunction that is embedded in the generalized Hilbert space [i.e., $(\vec{\phi}^Q)^2$ is integrable rather than $|\vec{\phi}^Q|^2$ as in the Hilbert space[10]].

We can summarize it by saying that by deriving the self-energy effective Hamiltonian for the closed channels rather than for the open channels, as had been done by Feshbach, we eliminated the open channels from our problem. By doing so we changed the wave boundary conditions for the original problem. The continuum states that are associated with the open channels are not scattering states and have outgoing wave boundary conditions as the boundary wave conditions for the bound states that are associated with the closed channels. This gives a convinced explanation for the text book result that an optical potential becomes a complex function for energies above the thershold.[15]

If one wishes to define a point where the formulation of quantum mechanics branches into the standard-Hermitian formulation and the non-Hermitian formulation, it is the point in our derivation where we decided to construct the effective Hamiltonian for the closed channels rather than for the open channels.

The question is, can E which solves eq 18 get a complex value $E = E_{\mathrm{r}} - \mathrm{i}/2\Gamma$ as proposed above?

The answer to this question is positive. $E = E_{\mathrm{r}} - (\mathrm{i}/2)\Gamma$ is a simple pole of the optical potential. Let us prove this claim. The spectral representation of $\mathbf{H}_{PP}$ is

$$\mathbf{H}_{PP} = \int_0^{+\infty} \mathrm{d}E_{\mathrm{c}}\, E_{\mathrm{c}}\rho(E_{\mathrm{c}})|\vec{\phi}^P_{E_{\mathrm{c}}}\rangle\langle\vec{\phi}^P_{E_{\mathrm{c}}}| \tag{23}$$

where E_{c} stands for the continuum energy spectrum of the open channels and $\rho(E_{\mathrm{c}})$ is the density of states in the continuum. When the continuum states are energy normalized such that $\langle E|E'\rangle = \delta(E - E')$, there is no need to introduce $\rho(E_{\mathrm{c}})$ into the integration over E_{c}. We introduce here $\rho(E_{\mathrm{c}})$ since we assume that the continuum eigenfunctions were calculated using the box-quantization condition while taking the limit of the box size to infinity. The use of the box-quantization condition will help us later in the derivation of the Fermi golden rule for the calculations of the resonance widths (inverse lifetime). By using the spectral representation of $\mathbf{H}_{PP}$, one gets that

$$E = \langle \phi^Q | \hat{H}_{QQ} | \phi^Q \rangle + \langle \vec{\phi}^Q | \mathbf{V}_{\mathrm{opt}}(\mathbf{R}, E) | \phi^Q \rangle = \langle \hat{H}_{QQ} \rangle + \int_0^{+\infty} \mathrm{d}E_{\mathrm{c}}\, \rho(E_{\mathrm{c}}) \langle \phi^Q | \mathbf{H}_{QP} | \phi^P_{E_{\mathrm{c}}} \rangle \times \langle \phi^P_{E_{\mathrm{c}}} | \mathbf{H}_{PQ} | \phi^Q \rangle \lim_{\epsilon \to 0+} \frac{1}{E - E_{\mathrm{c}} + \mathrm{i}\epsilon} \tag{24}$$

assuming that all poles of the Green function are a finite "distance" from the real E_c axis, then the contour of integration along the real E_c (E_c varies from 0 to ∞) can be replaced by a closed contour of integration in the complex E_c plane with the radius $|E_c^0|$ (i.e., E_c is varied from 0 to $2|E_c^0|$, and from this point return to the origin on the lower half of a circle the radius of which is $|E_c^0|$ and its center is on the real axis at $|E_c^0|$). The replacement of the contour of integration from a contour on the real axis to a closed contour in the complex plane is possible when the integrand is exponentially small in the lower E_c half-complex plane when $|E_c| > |E_c^0|$.

By using the definition of a delta function as the limit of a function that exhibits a sharp peak about E, while its integral over all space is equal to 1, one gets that

$$\lim_{\epsilon \to 0+} \frac{1}{E - E_{\mathrm{c}} + \mathrm{i}\epsilon} = \mathrm{PV}\frac{1}{E - E_{\mathrm{c}}} \mp \mathrm{i}\pi\delta(E - E_{\mathrm{c}}) \tag{25}$$

where PV stands for the (Cauchy) principle value.

By substituting eq 25 into eq 24 one obtains

$$E = \langle \vec{\phi}^Q | \hat{H}_{QQ} | \vec{\phi}^Q \rangle + \mathrm{PV} \int_0^{\infty} \mathrm{d}E_{\mathrm{c}}\, \rho(E_{\mathrm{c}}) \frac{|\langle \vec{\phi}^Q | \mathbf{H}_{QP} | \vec{\phi}^P_{E_{\mathrm{c}}} \rangle|^2}{E - E_{\mathrm{c}}} - i\pi\rho(E) \langle \vec{\phi}^Q | \mathbf{H}_{QP} | \vec{\phi}^P_E \rangle \langle \vec{\phi}^P_E | \mathbf{H}_{PQ} | \vec{\phi}^Q \rangle \tag{26}$$

Since eq 25 holds only for real values of E it implies that in the derivation of eq 26 we carry out an approximation where in the right-hand side of eq 26 we have to introduce the real part of E. Another approximation we can apply in order to simplify eq 26 is to assume the following.

(1) There is only one closed channel that supports a single bound state, $|E_b\rangle$ and in the right-hand side of eq 26 we can replace E by E_b since E is embedded close enough to the real axis [the resonance (metastable) state is a narrow resonance that has a sufficiently long lifetime to justify this approximation].

(2) There is only one open channel with the threshold energy $E_1^{\mathrm{th}} = 0$, and $\hat{H}_{PQ} := \hat{V}_{\mathrm{coup}}$. We also assume here that the continuum of the open channel is structureless. Namely, the density of states, $\rho(E_c)$, is varied monotonically with $E_c > 0$.

Under these assumptions, eq 26 is reduced to

$$E = E_{\mathrm{r}} - \frac{i}{2}\Gamma \tag{27}$$

where the resonance position is defined as $E_r = E_b + \Delta$ and the shift from the bound energy value is given by

$$\Delta = \mathrm{PV} \int_0^{\infty} \mathrm{d}E_{\mathrm{c}}\, \rho(E_{\mathrm{c}}) \frac{|\langle \vec{\phi}^Q | \hat{V}_{\mathrm{coup}} | \vec{\phi}^P_{E_{\mathrm{c}}} \rangle|^2}{E_{\mathrm{b}} - E_{\mathrm{c}}} \tag{28}$$

Let us calculate, for example, the value of the shift in the resonance position from the bound state energy in the closed channel for the case where the density of states in the continuum of the open channel is $\rho(E_c) = (1/E_c)^{1/2}$, the bound state in the closed channel is the ground-state of one-dimensional harmonic potential, and $\hat{V}_{\mathrm{coup}} = \varepsilon_0 x \exp(-(x/\sigma)^2)$, where σ is much larger than the size of the system which is under consideration (e.g., an atom, a molecule, or an artificial mesoscopic structure). The use of a one-dimensional model Hamiltonian for atoms in laser fields is commonly used in the literature, since the oscillating field breaks the spherical symmetric property of the atom and the electrons are ionized along the x-direction determined by the ac-field. In this model, $\hat{V}_{\mathrm{coup}}$ is the coupling between the bound state of the atom with the continuum due to the absorption of one photon only (no multiphoton absorption processes) when the weak ac-field is a cw linearly polarized light and therefore by using the dressed picture formalism one gets that ε_0 is the maximum field amplitude of the laser field divided by 2. A more detailed explanation is out of the scope of this paper. The Gaussian window function introduces into our calculations the fact that the laser beam has a finite width σ and therefore the dipole introduced by the laser field is effective only in a finite spatial region. For convenience, we use in solving this problem atomic units with $m_e = \hbar = 1 = a_0$, where the mass of the electron is m_e and the Bohr radius is defined as $a_0 = \hbar^2/(m_e e^2) = 1$. Therefore, $E_c = k_c^2/2$, where k_c is the wave vector of the continuum function of a free particle in the open channel. The threshold energy of the open channel is taken here as 0. Therefore, the bound state energy in the closed channel is positive, i.e., $E_b > 0$. Since the singularity in the expression for the resonance shift given in eq 28 is at $E_c = E$, the PV of the divergent integral is obtained by calculating the limit of the integral outside the interval $(E_b - \epsilon, E_b + \epsilon)$ as $\epsilon \to 0$. Namely, the shift in the resonance position from the bound state energy in the closed channel, E_b, is defined as

$$\Delta = \lim_{\epsilon \to 0} \left[\int_0^{E_{\mathrm{b}} - \epsilon} \mathrm{d}E_{\mathrm{c}} \frac{|\langle \phi^Q_{\mathrm{bound}} | \hat{V}_{\mathrm{coup}} | \phi^P_{E_{\mathrm{c}}} \rangle|^2}{\sqrt{E_{\mathrm{c}}}(E_{\mathrm{b}} - E_{\mathrm{c}})} + \int_{E_{\mathrm{b}+\epsilon}}^{\infty} \mathrm{d}E_{\mathrm{c}} \frac{|\langle \phi^Q_{\mathrm{bound}} | \hat{V}_{\mathrm{coup}} | \phi^P_{E_{\mathrm{c}}} \rangle|^2}{\sqrt{E_{\mathrm{c}}}(E_{\mathrm{b}} - E_{\mathrm{c}})} \right] \tag{29}$$

The ground bound state in the closed channel is defined as $\phi^Q_{\mathrm{bound}}(x) = (\alpha/\pi)^{1/4} \exp(-\alpha x^2/2)$.

Within the interval $-L/2 < x < +L/2$, where $L > 1/\alpha$ is the size of the system under consideration, $\hat{V}_{\mathrm{coup}} \simeq \varepsilon_0 x$. The matrix element $\langle \phi^Q_{\mathrm{bound}} | \hat{V}_{\mathrm{coup}} | \phi^P_{E_c} \rangle$ is equal to

$$\langle \phi^Q_{\mathrm{bound}} | \hat{V}_{\mathrm{coup}} | \phi^P_{E_{\mathrm{c}}} \rangle = \varepsilon_0 \int_{-\infty}^{+\infty} \mathrm{d}x \exp(-\alpha x^2/2) x \exp(+\mathrm{i}k_{\mathrm{c}}x) = \mathrm{i}\varepsilon_0 [2\sqrt{2\pi}/\alpha^{3/2}] k \exp(-0.5k^2/\alpha) \tag{30}$$

Therefore,

$$\Delta \simeq -\varepsilon_0^{\,2}[8\pi/\alpha^3] \lim_{\epsilon \to 0} \left[\int_0^{E_{\mathrm{b}} - \epsilon} \mathrm{d}E_{\mathrm{c}} \frac{\exp(-E_{\mathrm{c}}/\alpha)}{E_{\mathrm{b}} - E_{\mathrm{c}}} + \int_{E_{\mathrm{b}+\epsilon}}^{\infty} \mathrm{d}E_{\mathrm{c}} \frac{\exp(-E_{\mathrm{c}}/\alpha)}{E_{\mathrm{b}} - E_{\mathrm{c}}} \right] = -\varepsilon_0^{\,2}[8\pi/\alpha^3] \exp(-E_{\mathrm{b}}/\alpha) \mathrm{Ei}(E_{\mathrm{b}}/\alpha) \tag{31}$$

where Ei is the second exponential-integral function.[17]

The resonance width Γ (i.e., inverse lifetime) is given by

$$\Gamma = 2\pi\rho(E_b)|\langle\vec{\phi}^Q|\hat{V}_{\mathrm{coup}}|\vec{\phi}^P_{E_b}\rangle|^2 \tag{32}$$

where $\rho(E_b)$ is the density of states in the open channel. Here we neglect the shift of the resonance position from E_b. In the case of one-dimensional problems or in the case of three-dimensional problems with s-waves symmetry, or when the photoionization are induced by a linearly polarized laser that takes place primely along one direction, then $\rho(E_b) \simeq 1/\sqrt{E_b}$. Therefore, as the bound state in the closed channel approaches the threshold energy of the open channel Γ(Feshbach) → ∞ (provided $|\langle\vec{\phi}^Q|\hat{V}_{\mathrm{coup}}|\vec{\phi}^P_{E_b}\rangle|^2$ does not decay to zero faster or as fast as $\rho(E_b)$ when $E_b \to 0$). This behavior is very different from the behavior of the shape-type resonances, where the tunneling through the potential barrier is suppressed as the position of the resonance state approaches the threshold energy. We can have a better estimate for the value of the decay rate Γ of the Feshbach resonance as it touches from above the threshold energy of the open channel (just before it becomes a bound state) as E_b is varied by calculating the value of E_b for which $E_b + \Delta = 0$. Using the approximate expression for the Feshbach resonance position given in eq 32, we can estimate the value of E_b for which the resonance coincides with the threshold energy of the open channel. For example, for the value of $\alpha = 1$ the resonance position is at the threshold energy when $E_b = E_b^{\mathrm{th}} \equiv 0.28309$. Since $\rho(E_b^{\mathrm{th}})$ gets a finite value, then Γ(Feshbach) → finite value as well when the resonance position approaches the threshold energy of the open channel.

Equation 32 we obtained for Γ (i.e., the resonance decay rate which is inverse proportional to the resonance lifetime) is identical to the Fermi golden rule expression.

It is important to realize that the complex eigenvalues obtained by solving eq 19 with the non-Hermitian effective Hamiltonian given in eq 4 are also eigenvalues of the physical Hamiltonian given in eq 7. It implies that the corresponding eigenfunction is not in the Hilbert space as in the conventional (standard) formulation of quantum mechanics. The change of the boundary conditions in the solutions of the time-independent Schrödinger equation is "responsible" for the non-Hermitian property of the physical Hamiltonian. We may say that the solutions obtained in conventional quantum mechanics calculations are embedded in the Hermitian sector of the domain of the operator, whereas the resonance solutions are embedded in the non-Hermitian sector of the domain of the same physical operator.

It is a point of interest that the resonance solutions that are embedded in the non-Hermitian sector of the domain of the Hamiltonian are obtained from a very common application of the Green function method to the Hermitian (standard) formulation of quantum mechanics, where the outgoing boundary conditions are imposed by the Green operator.

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Appendix

As mentioned in the text, our proposition for a simple "point" where QM branches into the standard Hhermitian) formalism and the non-Hermitian formalism is based on the fact that the term $\mathrm{i}\epsilon$ in the Green operator where $\epsilon > 0$, i.e., $\hat{G}^+(E) = \lim_{\epsilon\to 0+}(E + \mathrm{i}\epsilon - \hat{H})^{-1}$, introduces outgoing wave boundary conditions on $|F\rangle = \hat{G}^+(E)|f\rangle$ for any wavepacket $|f\rangle$ that can be described as a linear combination of incoming and outgoing waves. For $\epsilon < 0$, the operation of the Green operator on a given wavepacket introduces incoming boundary conditions on $|F\rangle = \hat{G}^-(E)|f\rangle$. Although this fact is known (see, for example, ref 16), for the sake of coherency of our presentation, we explain it in this Appendix by emphasizing the role of the sign of ϵ.

The spectral representation of the Green operator is given by

$$\hat{G}^+(E) = \frac{1}{E + \mathrm{i}\epsilon - H'} = \int \mathrm{d}E' \frac{|\Psi_{E'}\rangle\langle\Psi_{E'}|}{E + \mathrm{i}\epsilon - E'} \tag{33}$$

where $\epsilon \to 0^+$ (we omit the use of $\lim_{\epsilon\to 0+}$ for brevity) and

$$\hat{H}\Psi_{E'} = E'\Psi_{E'} \tag{34}$$

The asymptote of the energy-normalized eigenfunctions $\Psi_{E'}$ consists of incoming and outgoing waves, $(2\pi k)^{-1/2}\exp(\mathrm{i}kx)$, which respectively are associated with negative and positive momentum $p = \hbar k$ and where $(\hbar k)^2/2 = E'$ (here we use for simplicity a one-dimensional Hamiltonian for noninteracting particles). We will use the atomic units where $m_e = \hbar = 1$. Since we wish to show that the asymptote of $\Phi = \hat{G}^+(E)\phi$ is an outgoing wavepacket we will calculate

$$\lim_{x\to\infty}\Phi(x) = \hat{\mathscr{G}}^+_\infty(E)\,\phi_\infty(x) \tag{35}$$

where, $\phi_\infty(x) = \lim_{x\to\infty}\phi(x)$, $\hat{\mathscr{G}}^+_\infty(E) = (E^+ + 0.5\,\mathrm{d}^2/\mathrm{d}x^2)^{-1}$, and $E^+ := E + \mathrm{i}\epsilon$. Therefore,

$$\lim_{x\to\infty}\Phi(x) = \int_{-\infty}^{+\infty}\mathrm{d}x'\,\mathscr{G}^+_E(x,x')\,\phi_\infty(x') \tag{36}$$

where

$$\begin{aligned}\mathscr{G}^+_E(x,x' &= (2\pi)^{-1}\int_{-\infty}^{+\infty}\mathrm{d}k\,\frac{\mathrm{e}^{\mathrm{i}k(x-x')}}{E^+ - k^2/2} \\ &= -\int_{-\infty}^{+\infty}\mathrm{d}k\,\mathrm{e}^{\mathrm{i}k(x-x')}\frac{1}{\sqrt{8E^+}}\left[\frac{1}{k-\sqrt{2E^+}} + \frac{1}{k+\sqrt{2E^+}}\right]\end{aligned} \tag{37}$$

Next we will employ the residue theorem

$$\int_{-\infty}^{+\infty}\mathrm{d}k\,\frac{\mathrm{e}^{\mathrm{i}k(x-x')}}{\sqrt{2E^+} \pm k} = -2\pi\mathrm{i}\mathrm{e}^{\mp\mathrm{i}\sqrt{2E^+}(x-x')} \tag{38}$$

Notice that $\exp[-\mathrm{i}(2E^+)^{1/2}(x - x')] \to 0$ when $x \le x'$ and that it exponentially diverges when $x > x'$. Conversely, $\exp[+\mathrm{i}(2E^+)^{1/2}(x - x')] \to 0$ when $x > x'$ and it exponentially diverges when $x \le x'$. Consequently, by applying the Green operator on the square-integrable wavepacket

$$\lim_{x\to\infty} \Phi(x) = \frac{1}{\mathrm{i}\sqrt{8E}} \mathrm{e}^{+\mathrm{i}\sqrt{2E}x} \Big[\int_{-\infty}^{x} \mathrm{d}x' \, \mathrm{e}^{\mathrm{i}\sqrt{2E^+}x'} \phi_\infty(x') + \mathrm{e}^{-2\mathrm{i}\sqrt{2E}x} \int_{x}^{\infty} \mathrm{d}x' \, \mathrm{e}^{-\mathrm{i}\sqrt{2E^+}x'} \phi_\infty(x') \Big] \quad (39)$$

Since as $x \to \infty$ the second term in the right-hand side of eq 39 vanishes, then

$$\lim_{x\to\infty} \Phi(x) = \frac{1}{\mathrm{i}\sqrt{8E}} \Big[\int_{-\infty}^{+\infty} \mathrm{d}x' \, \mathrm{e}^{\mathrm{i}\sqrt{2E}x'} \phi_\infty(x') \Big] \mathrm{e}^{+\mathrm{i}\sqrt{2E}x} \quad (40)$$

Equation 40 shows that the wave packet $\Phi = \hat{G}^+(E)\phi$ indeed is constructed of outgoing waves only. This completes the proof that the $+\mathrm{i}\epsilon$ in the Green operator, $\hat{G}^+(E) = \lim_{\epsilon\to 0+}(E + \mathrm{i}\epsilon - \hat{H})^{-1}$ introduces outgoing wave boundary conditions on $\Phi = \hat{G}^+(E)\phi$.

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