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"NEW" MOLECULAR BOUND AND RESONANCE STATES

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It has been shown previously that a new type of molecular bound state can result from corrections to the Born-Oppenheimer approximation. It is shown here that "new" bound and resonance states can occur in a variety of problems involving coupled wave equations. Several examples are discussed, the most important one involving the bound and resonance states of van der Waals complexes.

A. INTRODUCTION

Some years ago, it was pointed out that non-adiabatic coupling between two diatomic electronic states can lead to "new" bound vibrational states (1,2). If a purely repulsive potential energy curve which supports no bound states is coupled in a particular way to an excited potential which does support bound states, a new bound state can occur with an energy below the dissociation limit of the repulsive curve. Apparently there have been no experimental observations of such a state, and indeed, the conditions for observing and recognizing its effects in spectral data are very stringent (2,3).

New bound states may arise not only in systems which violate the Born-Oppenheimer separation, but also in scattering processes involving a single Born-Oppenheimer potential surface. We discuss this situation in this paper, and show that concomitant with the new bound states are "new" resonance states in the continuum. In addition, we discuss the possibility of new resonance states due to non-adiabatic coupling of two repulsive Born-Oppenheimer potentials, neither of which supports bound states. "New" resonance may occur, particularly when the interaction between them is localized and strong. The coupling of continuum states resulting in a bound state is well-known in the theory of superconductivity (4).

Of course, a state of a system can be designated as "new" only with reference to an approximate description of the system in which the state in question is absent in the first approximation. When it

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appears at a higher level of approximation, it is termed "new".

The descriptions we are considering are based on sets of coupled wave equations which result from averaging a complete wave equation over all degrees of freedom but one of special interest. Denoting this special degree of freedom by R and all others by r, the assumed form of the exact wavefunction is

$$\Psi_\alpha(R,r) = \sum_n \chi_{n\alpha}(R) \, \phi_n(r,R) \qquad (1)$$

where the ϕ_n are some fixed basis functions which are complete and orthonormal in the variables r, and the $\chi_{n\alpha}$ are functions to be determined from the wave equation. For simplicity, we shall assume that the ϕ_n are real functions. In the Born-Oppenheimer approximation for a diatomic molecule, the r are the electronic coordinates and R is the internuclear separation. In the scattering problem on a single Born-Oppenheimer potential, the R is the intermolecular separation, and the r are the internal degrees of freedom (rotations, vibrations) of the scattering molecules plus the overall rotational degrees of freedom of the complex.

Substitution of the wavefunction Ψ_α into the wave equation leads to a set of coupled equations for the functions $\chi_{n\alpha}$,

$$(\hat{T}_R + V_{nn}(R) - E_\alpha)\chi_{n\alpha}(R) + \sum_m V_{nm}(R) \, \chi_{m\alpha}(R) = 0 \qquad (2)$$

where $\hat{T}_R$ is the kinetic energy operator for R and $V_{nm}(R)$ is the matrix element of the Hamiltonian in the basis $\phi_n(r,R)$.

If all of the off-diagonal elements V_{nm} are small, the essential features of the problem are revealed by neglecting them completely and solving the resulting uncoupled equations. The "ordinary" bound states are obtained at this level of approximation. "New" bound states may result when the off-diagonal elements are considered, as discussed previously (1-3) and in the next section of the present paper.

The form of the wavefunction, Eq. (1), is not unique (5-7), however, since it is invariant to an R-dependent orthogonal transformation of the ϕ_n. Such a transformation leads to coupled equations of the same form as Eq. (2), but with redefined potentials V_{nm} and hence a different definition of what are "ordinary" and what are "new" bound states. Thus, "new" bound states are new only with respect to a particular choice of basis functions ϕ_n, and may be recast as "ordinary" bound states by a proper choice of basis.

B. "NEW" BOUND STATES

In this section we review the analysis (2,3) which provides the condition for a "new" bound state to appear at a particular stage in a sequence of approximate solutions to Eq. (2).

We assume that the first level of approximation is to neglect all off-diagonal potentials in Eq. (2). This gives a set of uncoupled equations,

$$(\hat{T}_R + V_{nn}(R) - E_{n\alpha}^0)\chi_{n\alpha}^0(R) = 0 \tag{3}$$

which may be solved for a set of eigensolutions $(E_{n\alpha}^0, \chi_{n\alpha}^0)$ for each potential $V_{nn}(R)$. For convenience of notation, we shall assume a box normalization $[0 \leq R \leq R_{max}, \chi_{n\alpha}(R_{max}) = 0]$, so that the continuous spectrum of $(\hat{T}_R + V_{nn}(R))$ is represented by a closely-spaced sequence of eigenvalues. At the end of the discussion we may consider the limit $R_{max} \to \infty$. The case we wish to consider is when the lowest potential $V_{00}(R)$ [i.e. $V_{00}(R_{max}) \leq V_{nn}(R_{max})$, $n > 0$] supports no bound states, $E_{n\alpha}^0 \geq V(R_{max})$, all α, as shown in Figure 1.
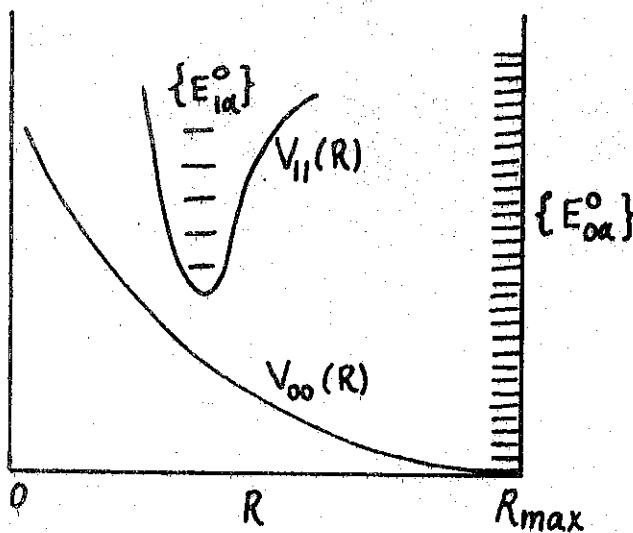

Figure 1. Potential Curves and Eigenenergies for Discussion of New Bound States.

Each of the sets of eigenfunctions $\{\chi_{n\alpha}^0(R)$, n fixed, $\alpha = 0,1,2,\ldots\}$ is assumed to provide a complete basis, so that in higher levels of approximation where the off-diagonal potentials in

Eq. (2) are not neglected, each $\chi_{n\alpha}$ may be expanded in terms of the corresponding set $\{\chi_{n\alpha}^0\}$,

$$\chi_{n\alpha}(R) = \sum_\beta c_{n\beta}^\alpha \chi_{n\beta}^0(R) . \tag{4}$$

These expansions transform the coupled wave equations (2) into a set of coupled algebraic equations,

$$(E_{n\beta}^0 - E_\alpha)c_{n\beta}^\alpha = -\sum_{m\gamma} V_{n\beta,m\gamma} c_{m\gamma}^\alpha \tag{5}$$

where

$$V_{n\beta,m\gamma} = \langle \chi_{n\beta}^0 | V_{nm} | \chi_{m\gamma}^0 \rangle . \tag{6}$$

A sequence of approximations may be defined in which more and more terms are included in the summation in Eq. (5).

At any level of approximation, the solution of the set of Eqs. (5) is conveniently discussed in terms of familiar partitioning techniques (8). At the second level of approximation, only two sets, n = 0 and 1, are included in Eqs. (5),

$$(E_{0\beta}^0 - E_\alpha)c_{0\beta}^\alpha = -\sum_\delta V_{0\beta,1\delta} c_{1\delta}^\alpha \tag{7a}$$

$$(E_{1\gamma}^0 - E_\alpha)c_{1\gamma}^\alpha = -\sum_\beta V_{1\gamma,0\beta} c_{0\beta}^\alpha . \tag{7b}$$

Solving the first equation for $c_{0\beta}^\alpha$ and substituting the result into the second yields

$$(E_{1\gamma}^0 - E_\alpha)c_{1\gamma}^\alpha - \sum_{\beta\delta} V_{1\gamma,0\beta}(E_{0\beta}^0 - E_\alpha)^{-1} V_{0\beta,1\delta} c_{1\delta}^\alpha = 0 . \tag{8}$$

The eigenvalue condition for E_α is that the determinant of coefficients of the $c_{1\gamma}^\alpha$ vanishes, which may be written

$$\det\{\delta_{\gamma\delta}(E_{1\gamma}^0 - E_\alpha) - \sum_\beta V_{1\gamma,0\beta}(E_{0\beta}^0 - \mathcal{E})^{-1} V_{0\beta,1\delta}\} = 0 \tag{9a}$$

and

$$E_\alpha(\mathcal{E}) = \mathcal{E} . \tag{9b}$$

The general properties of the functions $E_\alpha(\mathcal{E})$ are well-known (8). For $\mathcal{E}$ large and negative each E_α approaches one of the eigenvalues $E_{1\gamma}^0$. In addition each E_α is a monotonically decreasing function of $\mathcal{E}$ with poles at the eigenvalues $E_{0\beta}^0$, which in the present application are closely spaced points on the positive energy axis representing the continuum of eigenvalues of $(\hat{T}_R + V_{00}(R))$. Hence a graphical solution of Eq. (9) has the qualitative appearance shown in Figure 2
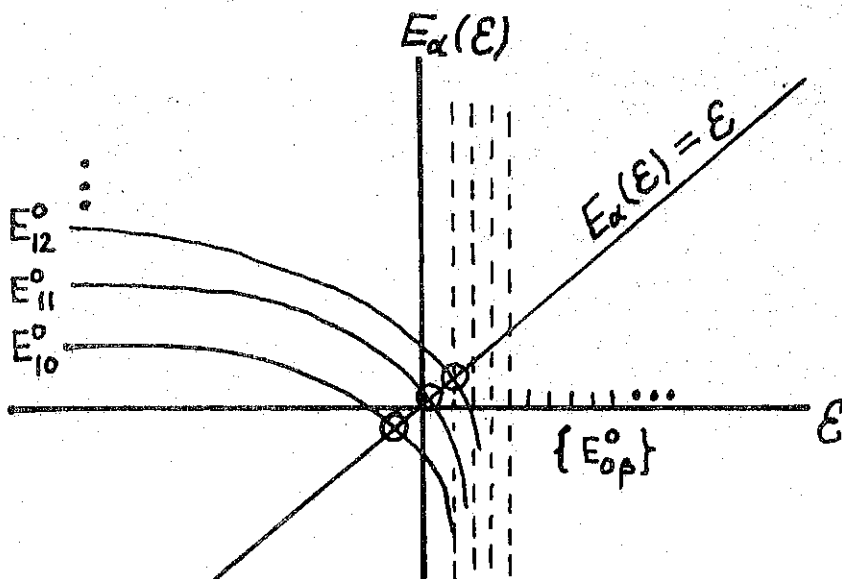

Figure 2. Qualitative behavior of $E_\alpha(\mathcal{E})$. The circles denote points at which the eigenvalue condition, Eq. (9), is satisfied.

"New" bound states correspond to eigenvalues $E_\alpha < 0$. It is clear from Figure 2 that for any finite R_{max} the number of such states is given by the number of negative eigenvalues $E_\alpha(0)$; that is, the number of negative roots of the secular equation,

$$\det\{\delta_{\gamma\delta}(E_{1\gamma}^0 - E_\alpha(0)) - \sum_\beta V_{1\gamma,0\beta} V_{0\beta,1\delta} / E_{0\beta}^0\} = 0 , \tag{10a}$$

$$E_\alpha(0) < 0 . \tag{10b}$$

These two equations are the general conditions for "new" bound states to appear at the second level of approximation. In principle we should consider the limit $R_{max} \to \infty$; however, since each eigenvalue $E_\alpha(\mathcal{E})$ is

expected to be a decreasing function of R_{max}, the number of "new" bound states for a finite R_{max} is an upper bound to the true number.

Further analysis depends on the particular nature of the problem under consideration, as this determines the magnitudes of the matrix elements appearing in Eq. (10). Previous analysis (2,3,7) has focussed on problems involving the Born-Oppenheimer separation and will not be repeated here. In the following sections, examples such as arise in scattering problems will be discussed.

General qualitative conditions for "new" bound states can be given from an examination of Eq. (10). If the coupling matrices $V_{1\alpha,0\beta}$ are small, it is clear that E_{10}^0 must also be small (i.e. close to threshold). If there are a number of small eigenvalues $E_{1\gamma}^0$, or if the coupling elements are large, then there may be a number of "new" bound states. This apparently does not happen in Born-Oppenheimer problems (2), but it may in scattering problems. Finally, if the set of eigenvalues $E_{1\gamma}^0$ also are a discrete representation of a continuum, "new" bound states may appear which persist in the limit $R_{max} \to \infty$.

We turn now to a discussion of a few examples. Although these are model problems, they exhibit the qualitative behavior found in real scattering problems.

C.   EXAMPLES

a.   A Spin Problem

It is instructive to consider first an exactly soluble model problem corresponding to the idealized Stern-Gerlach experiment illustrated in Figure 3.
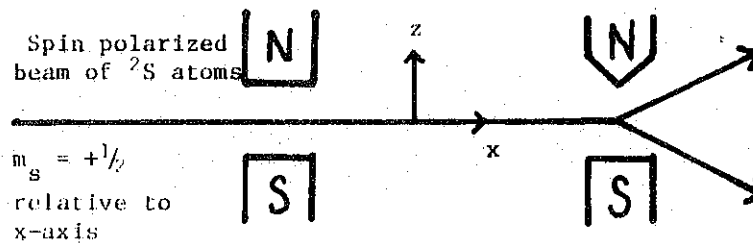

Figure 3.   Modified Stern-Gerlach Experiment. The left magnetic field
            is homogeneous, while the second (Stern-Gerlach) field is
            inhomogeneous.

A polarized beam of paramagnetic ^{2}S atoms whose spins are quantized ($m_s = +1/2$) with respect to the laboratory x-axis enters a region of

homogeneous magnetic field oriented in the z-direction. With respect
to the z-axis of quantization, the beam contains equal components of α
and β spin. For the α-component, the homogeneous magnetic field
presents a square barrier and the scattering of the wave packet will
show reflection, transmission, and for certain energies, resonances.
For the transmitted α-component there will be a time-delay which may be
long in the vicinity of resonances. For the β-component, the
homogeneous field presents a square well which may support a number of
bound states, and the transmitted component will be accelerated,
particularly in the vicinity of resonances. Thus, as the beam emerges
from the homogeneous field region, it will have unequal α and β spin
components with respect to the z-axis of quantization, so the
Stern-Gerlach magnet will split the beam into two, with the relative
intensities of the two beams depending on the kinetic energy of the
beam and the strength of the homogeneous magnetic field.

The quantum mechanical description of this spin scattering
experiment involves solving the wave equation for the stationary state
of the Hamiltonian for the system in the region of homogeneous magnetic
field.

$$\hat{H} = (p^2/2m) + \lambda \vec{B} \cdot \vec{S} \tag{11}$$

where the first term is the atomic kinetic energy and the second the
magnetic interaction of the spin with the homogeneous field. In the
central region

$$\vec{B} = B(x)\hat{z} \tag{12}$$

where $B(x)$ vanishes except between the pole faces of the central
magnet, where it has a constant value. If the stationary state
eigenfunctions of H are expressed in terms of spin-components quantized
along the x-axis, the wave equation is equivalent to two coupled
equations

$$(\frac{p^2}{2m} - E)\psi_\alpha^x = \lambda B \psi_\beta^x \tag{13a}$$

$$(\frac{p^2}{2m} - E)\psi_\beta^x = \lambda B \psi_\alpha^x . \tag{13b}$$

With this quantization, ψ_α^x and ψ_β^x may be viewed as two free particle
scattering states which are coupled by a localized interaction $\lambda B(x)$.
The fact that this coupling can give rise to "new" bound and resonance
states is obvious if instead we express the wavefunction in terms of
spin-components quantized along the z-axis. Then the two
spin-components are uncoupled and satisfy the equations

$$(\frac{p^2}{2m} + 1/2 \; \lambda B(x) - E)\psi_\alpha^z \; = \; 0 \qquad\qquad (14a)$$

$$(\frac{p^2}{2m} - 1/2 \; \lambda B(x) - E)\psi_\beta^z \; = \; 0 \qquad\qquad (14b)$$

the solutions of which are discussed in many textbooks (9). The second equation may possess a number of bound states (10) depending on the strength and width of the magnetic field, while both equations exhibit resonances for positive energies.

Thus, the existence of "new" bound and resonance states is revealed in this spin example by a unitary transformation of the hamiltonian which diagonalizes the potential matrix. A special feature of this model is the fact that the unitary transformation commutes with the kinetic energy operator so that the transformed equations are completely uncoupled. In the general case, the transformed equations, which exhibit the "new" bound states explicitly, are a better first approximation than the original set.

b. Atom-Diatomic Molecule Scattering

A common class of problems where "new" bound states can occur involves atom-diatom scattering on a single Born-Oppenheimer potential surface. It is conventional in such problems to represent the surface in terms of Legendre polynomials,

$$V(R,\theta) \; = \; \sum_{\ell=0} \; V_\nu(R) \; P_\ell(\cos\theta) \qquad\qquad (15)$$

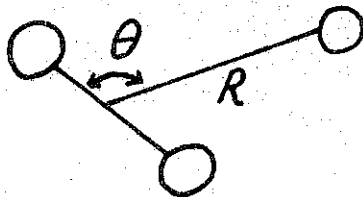where the variables are defined in Figure 4.

Figure 4. Variables for Atom-Diatom Scattering.

The scattering wavefunction is obtained as a solution to a set of coupled equations of the form of Eq. (2), where the variables r which have been averaged correspond to the vibration and rotation of the diatomic, and the rotation of the triatomic complex as a whole. The

c. "New" Resonance States

So far we have discussed mainly the appearance of "new" bound
states. We now give a simple example to show that "new" resonance
states are expected to accompany the occurrence of "new" bound states.
Consider the pair of coupled equations

$$[\frac{p^2}{2m} + V_{00}(R) - E]\chi_0(R) + V_{01}(R)\chi_1(R) = 0 \tag{20a}$$

$$[\frac{p^2}{2m} + V_{11}(R) - E]\chi_1(R) + V_{01}(R)\chi_0(R) = 0 \tag{20b}$$

where $V_{00}(R)$, $V_{01}(R)$, and $V_{11}(R)$ have the qualitative appearance shown
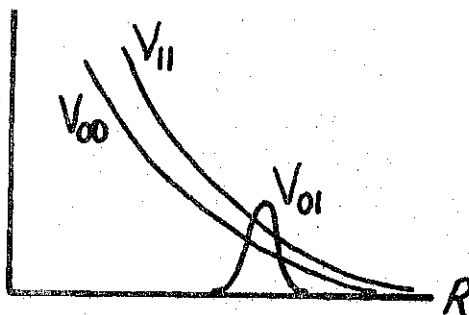in Figure 5a

Figure 5a.   Potential Functions appearing in Eq. (20).

These equations may arise, for example, by truncating the equations for
our atom-diatom scattering problem such as was discussed previously.

If we transform the basis, for example by the R-independent
transformation,

$$\chi_0' = (\chi_0' + \chi_1')/\sqrt{2} \tag{21a}$$

$$\chi_1' = (\chi_0' - \chi_1')/\sqrt{2} \tag{21b}$$

then we obtain new potentials

$$V'_{00} = 1/2(V_{00} + V_{11}) - V_{01} \qquad (22a)$$

$$V'_{11} = 1/2(V_{00} + V_{11}) + V_{01} \qquad (22b)$$

$$V'_{01} = 1/2(V_{00} - V_{11}) \qquad (22c)$$

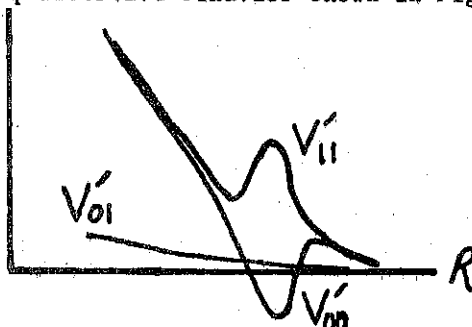which have the qualitative behavior shown in Figure 5b

Figure 5b. Transformed Potentials Resulting from the Transformation
Eq. (21).

If the equations are decoupled by neglecting V'_{01}, the potential V'_{11} can have shape resonances which persist even when V'_{01} is subsequently included. When these equations are appropriate for treating van der Waals molecules, the "new" resonance states are presumably associated with the temporary trapping of the scattering atom in the potential well of the diatomic.

D. SUMMARY

We have seen that "new" bound and resonance states may arise in a variety of problems involving sets of coupled wave equations. The identification of a state as "new" results from a particular choice of approximate wavefunction, and a "new" state may be transformed into an "ordinary" one by the proper change of basis. Although "new" states resulting from deviations from the Born-Oppenheimer separation are expected to be extremely rare, they may be more common in molecular scattering events.

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10. Of course, these states are unbound in the suppressed y-direction.