Many-Body Coulomb Problem in the Phase-Energy Representation

John L. Bohn

Abstract
The many-body quantum-mechanical Coulomb problem is exactly reformulated in a "phase-energy" representation. Rather than solving for a many-component wave-function, this formulation focuses on a set of eigenphases that document the evolution of a system from its compact to its fragmented limit. The eigenphases in turn hinge on the explicit evaluation of kinetic and potential energies as the system evolves. An illustration using the doubly excited states of helium shows that information on the nature of the eigenchannels is encoded in these energies.

Key words: many-body Coulomb dynamics, phase-energy representation, eigenphases, R-matrix evolution, hyperspherical coordinates

1. A MAN WITH A PLAN: FANO AND THE HYPER-RADIUS

Nearly 20 years ago Ugo Fano published his vision of a unified picture of atomic and molecular physics.\(^1\) In this view the dynamics of interacting electrons and nuclei centers on the competition between kinetic energies that dominate at small length scales, and Coulomb energies that dominate at large scales. This change of emphasis between the two competing agents dictates the transition of a system of particles from its compact to its fragmented limits, including the branching ratio for various outcomes. These transitions are moreover expected to occur abruptly at localized values of a suitable reaction coordinate.\(^1\)\(^2\) Any atomic or molecular phenomenon—bound states, scattering, ionization, dissociation, chemical reactions, etc.—can be formulated in terms of this fundamental competition.

The length scale on which a transition from centrifugal to Coulomb dominance occurs depends of course on the total energy and on the phenomena considered. To deal flexibly with a variety of length and energy scales, Fano proposed parameterizing the size of an \(N\)-body system using the now-famous hyperradius \(R\), defined as the system's radius of inertia:

\[
R^2 = \frac{1}{M} \sum_{i=1}^{N-1} m_i r_i^2, \quad M = \sum_{i=1}^{N-1} m_i, \tag{1}
\]

for an appropriate set of Jacobi coordinates \(r_i\) and reduced masses \(m_i\). Dynamical effects are then viewed as the change in the wave-function or related quantities as the hyperradius "evolves" from small to large values. This evolutionary concept, which regards \(R\) as analogous to a time-like coordinate, is central to Fano's viewpoint; we will also adopt it here.\(^1\)

Mathematically \(R\) represents the radius of a hypersphere in the 3\((N-1)\)-dimensional coordinate space of a system with 3\((N-1)\) degrees of freedom. The remaining coordinates, collectively denoted as \(\vec{R}\), are then angular coordinates on the hypersphere, and may be parameterized in a variety of ways.\(^3\) Regardless of their parameterization, however, the Hamiltonian for an \(N\)-body system interacting via Coulomb potentials takes a unified form (we will use atomic units throughout)

\[
- \frac{1}{2M} \left[ \frac{1}{R^{3N-1}} \frac{\partial}{\partial R} \left( R^{3N-1} \frac{\partial}{\partial R} \right) - \frac{\Lambda^2}{R^2} \right] + \frac{C(\vec{R})}{R}. \tag{2}
\]

Here \(\Lambda^2/2MR^2\) stands for a generalized centrifugal energy, and \(C(\vec{R})/R\) for the configuration-dependent Coulomb energy at fixed hyperradius.\(^1\) The form of the Hamiltonian in (2) emphasizes the centrifugal-vs.-Coulomb conflict that arises as \(R\) grows, shifting dominance from the \(1/R^2\) term to the \(1/R\) term. This process is enriched by the fact that the operators \(\Lambda^2\) and \(C(\vec{R})\) fail to commute, implying that the physical channels themselves transform from eigenstates of \(\Lambda^2\) at small values of \(R\) to eigenchannels of \(C(\vec{R})\) in the large-\(R\) fragmentation limit.\(^1\)

The hyperspherical viewpoint has proven remarkably flexible in understanding several-body physics. Among its greatest successes is the quantum-mechanical treatment of Wannier double ionization near threshold.\(^4-6\) In addition, by treating \(R\) as an adiabatic parameter, effective potentials and approximate wave-functions are obtained that enable a complete classification of the doubly excited states of...
two-electron atoms \cite{7,8} as well as larger atoms with two valence electrons \cite{9}. In the hands of C.D. Lin and coworkers this work is now progressing to the classification of three-electron atoms \cite{10}.

Further developments, also spearheaded by Fano, aim at going beyond an adiabatic approximation, to treat the exact equations of motion in $R$ in such a way that the centrifugal-to-Coulomb transition is still made apparent. These developments are based on the variable-phase approach of Calogero, which seeks insight into the values of observable phase shifts by exploring their $R$ dependence.\cite{11}

This idea has led to computational methods that track either eigenphase shifts\cite{12} or else total eigenphases\cite{13} as a function of $R$. The significant regions of $R$ where new channels are created and populated are then manifested either by the $R$ dependence of the phases, or else in avoided crossings of the phases. A key ingredient in these methods is that the solutions to Schrödinger’s equation are constructed stepwise, from one value of $R$ to the next, in a way dictated by the problem itself.

Nevertheless, it seems we have a long way to go before realizing Fano’s vision of a complete hyperspherical treatment of complicated scattering processes such as chemical reactions. This is due in part to the sheer complexity of these problems, where many channels are energetically available. Following these channels requires a complete solution of the Schrödinger equation in all $3(N - 1)$ coordinates in addition to the hyperradius.

In this essay I outline a method for expanding the use of hyperspherical coordinates to more elaborate problems in chemical physics. This method is an offspring of the eigenphase methods noted above, but casts the problem entirely in terms of an appropriate set of eigenchannels. Its key novelty is to remove the explicit dependence of the equations of motion on the hyperangular coordinates $\hat{R}$ except as an initial condition that can be handled once and for all. Quantum-mechanical evolution is instead described by explicit consideration of the partition of energy between its kinetic and potential components.

2. MODUS OPERANDI

2.1 R-matrix Evolution

The first step in tracking the evolution of the multiparticle wave-function from small to large $R$ is to establish its behavior at small $R$. As is well known these solutions are the hyperspherical harmonics, i.e., eigenfunctions $Y_\beta(\hat{R})$ of the centrifugal operator $\Lambda^2$.\cite{13} The index $\beta$ will stand here for the several indices needed to specify each harmonic, including he generalized centrifugal quantum number $\lambda$ in the eigenvalue equation

$$\Lambda^2 Y_\beta(\hat{R}) = \lambda (\lambda + 3N - 2) Y_\beta(\hat{R}).$$ \hspace{1cm} (3)

The full wave-function $\Psi$ is then expanded into harmonics:

$$R^{(3N-1)/2} \Psi_\beta(\hat{R}, \vec{r}) = \sum_\beta Y_\beta(\hat{R}) F^\beta_\beta(\vec{R}),$$ \hspace{1cm} (4)

where the index $\beta_0$ denotes the harmonic to which $\Psi_\beta$ reduces in the $R \to 0$ limit. The radial functions $F$ then satisfy a set of coupled-channel Schrödinger equations

$$\frac{d^2 F^\beta_\beta}{dR^2} + \sum_\beta k^2_{\beta\beta}(R) F^\beta_\beta(R) = 0.$$ \hspace{1cm} (5)

The coupling is given by matrix elements of the squared wave-number operator, which represents the hyperradial kinetic energy with which the system is expanding:

$$k^2_{\beta\beta}(R) = \frac{1}{\hbar^2} \int d\hat{R} Y_\beta(\hat{R})$$

$$\times \left[ \frac{\Lambda^2 + (3N - 4)(3N - 6)/4}{R^2} - \frac{2M C(\hat{R})}{R} \right] Y_\beta(\hat{R}).$$ \hspace{1cm} (6)

where $E$ denotes the system’s total energy. At this point the matrices $\Lambda^2_{\beta\beta}$ and $C_{\beta\beta}$ are independent of $R$, and in fact $\Lambda^2_{\beta\beta}$ is diagonal in the $\beta$ basis. In the following, however, we will have occasion to consider the corresponding matrices in an $R$-dependent basis, which will make explicit the competition between centrifugal and Coulomb energies.

The direct solutions of (5) are not terribly illuminating in themselves, since in general a large number of channels $\beta$ are needed to give physical solutions. Indeed, the hyperspherical harmonics are well known to fall numerically in the large-$R$ limit in ionization channels. A typical next step would then be to diagonalize $k^2_{\beta\beta}$ at each value of $R$ to produce the adiabatic channels, although even this procedure needs to be complemented by asymptotic solutions.\cite{14}

For our present derivation, however, we only require that the hyperspherical harmonics in principle form a complete set on the surface of the hypersphere.

In order to follow the evolution of our dynamical system as a function of $R$, Ref. 13 found it convenient to recast the coupled-channels problem in terms of eigenchannels of an $R$-dependent R-matrix $\mathcal{R}$, defined by

$$\sum_\beta \mathcal{R}_{\beta\beta}(R) \frac{d^2 F^\beta_\beta}{dR^2} - F^\beta_\beta = 0.$$ \hspace{1cm} (7)

Diagonalizing $\mathcal{R}$ at each value of $R$.
Many-Body Coulomb Problem in the Phase-Energy Representation

\[ \mathcal{R}_{p\rho} (R) = \sum_{\rho'} \langle \rho' | \rho(R) \rangle \tan \phi_{\rho}(R) \langle \rho | \rho(R) | \rho' \rangle. \quad (8) \]

yields a selection of eigenphases \( \phi_{\rho}(R) \) each describing
the radial evolution of an eigenchannel \( | \rho(R) \rangle \). Ref. 13 further
derives the equations of motion for the eigenphases and

eigenchannels, as follows:

\[ \frac{d \phi_{\rho}}{dR} = \cos^2 \phi_{\rho} + k_{p\rho}^2 \sin^2 \phi_{\rho}, \quad (9) \]

\[ \frac{d \langle \rho | \beta \rangle}{dR} = \sum_{\rho' \neq \rho} \frac{\sin \phi_{\rho} k_{p\rho} \sin \phi_{\rho'}}{\sin(\phi_{\rho} - \phi_{\rho'})} \langle \rho' | \beta \rangle. \quad (10) \]

Here the squared wave-number matrix is recast in the

evolving eigenbasis by

\[ k_{p\rho'}^2 = \sum_{\beta \rho} \langle \beta | \rho \rangle k_{p\rho}^2 \langle \beta' | \rho' \rangle. \quad (11) \]

The effect of these manipulations is to reduce the full

problem as far as possible to a collection of single-channel

problems. The difference here is that, via (10), each channel

| \rho \rangle is being "made up as it goes along," based on its coupling
to the other eigenchannels. In this way the solution deter-
mines its own set of appropriate channels that adequately
balance the centrifugal and Coulomb energies.

2.2 Removal of the Basis Set

We come now to the meat of this essay. The evolution

equations (9) and (10) still present a practical problem, since

they refer explicitly to the basis set | \beta \rangle. As noted above,

literally expanding into hyperspherical harmonics can be a

numerical disaster for any interesting problem. It is possible,
of course, to derive the equivalent equations of motion using an

adiabatic basis rather than the diabatic | \beta \rangle basis; how-
ever, doing so still presents the question of how to obtain
accurate adiabatic channel functions in a many-body

problem.

The resolution to this problem is already in front of us:
since we have a set of physically motivated channel functions

| \rho \rangle, we should employ them to pursue the calculation. We

will see that this bypasses any explicit consideration of the
basis set, replacing it instead with explicit consideration of the
centrifugal and Coulomb energies themselves.

To begin, note that (9) for the eigenphase is almost
self-contained, if only we knew the behavior of the squared

wave-number \( k_{p\rho}^2 \) in this channel. But this kinetic energy is

simply the deficit between the total energy \( E \) at which we are
performing the calculation and the total centrifugal plus

Coulomb energy. Thus what is required is to evaluate the \( \mathcal{R} \)
de
dependence of the matrix elements \( \Lambda_{p\rho}^2 \) and \( C_{p\rho} \), evaluated

in the eigenchannel basis.

To perform this evaluation, consider for example the

Coulomb energy. Expanding \( C_{p\rho} \) into the \( R \)-independent basis

| \beta \rangle, and recalling that \( C_{p\rho} \) is itself \( R \)-independent, we find the derivative

\[ \frac{d C_{p\rho}}{dR} = \sum_{\rho' \neq \rho} \left( \frac{d \langle \rho | \beta \rangle}{dR} C_{p\rho} \langle \beta | \rho' \rangle + \langle \rho | \beta \rangle C_{p\rho} \frac{d \langle \beta | \rho' \rangle}{dR} \right). \quad (12) \]

The derivatives of the eigenchannels are removed using the

evolution equation (10) and its adjoint, yielding the expres-
sion for \( \mathcal{C} \)

\[ \frac{d C_{p\rho}}{dR} = \sum_{\rho'} \left( k_{p\rho}^2 C_{\rho \rho'} - C_{p\rho} \tilde{k}_{p\rho}^2 \right). \quad (13) \]

We introduce for notational simplicity we denote the "phase-
dressed" squared wave-number by

\[ \tilde{k}_{p\rho}^2 = \begin{cases} \frac{\sin \phi_{\rho} k_{p\rho} \sin \phi_{\rho'}}{\sin(\phi_{\rho} - \phi_{\rho'})}, & \rho \neq \rho', \\ 0, & \rho = \rho'. \end{cases} \quad (14) \]

In exactly the same way we arrive at the evolution equation

for the centrifugal portion:

\[ \frac{d \Lambda_{p\rho}^2}{dR} = \sum_{\rho'} \left( \tilde{k}_{p\rho}^2 \Lambda_{\rho' \rho}^2 - \Lambda_{p\rho}^2 \tilde{k}_{p\rho'}^2 \right). \quad (15) \]

Equations (13)–(15), together with the phase equation (9),
constitute the main new result of this essay. We stress that
these equations constitute an exact reformulation of the
Coulomb many-body problem in (5). The novelty is that we can
now evolve the system from small to large values of \( R \)
without explicit reference to any external basis set, either
diabatic or adiabatic. This is accomplished by focusing not on
the many degrees of freedom encompassed in the coordi-
nates \( \bar{R} \), but on the overall structure of the eigenmodes, and
the way they affect the various energy scales in the problem.
In so doing we have identified the partition of the total
energy \( E \) into three key components: the centrifugal energy
\( \Lambda_{p\rho}^2/2MR^2 \), the Coulomb energy \( C_{p\rho}/R \), and the "leftover"
outward kinetic energy \( k_{p\rho}^2/2M \) in each channel. Since the
dynamical elements of the theory are now eigenphases and energies, we refer to this formulation as the “phase-energy” representation.

This formulation of the many-body problem deliberately discards the wave-function and along with it the possibility of visualizing particle correlations by mapping density profiles or equivalent features. Nevertheless, in a system of sufficiently many particles such maps will themselves be difficult to disentangle since they involve many degrees of freedom. Exceptions of course occur in states with a high degree of symmetry or with only a couple of active constituents. But in general a full representation of a many-body wave-function is difficult to grasp for human minds that operate in three dimensions only. Rather, it is expected that physical insight will come from mapping the R dependence of the energy partition into the three components listed above. For example, if the effective charge C_{eff} is found to settle in to a particular value, it probably indicates that the corresponding eigenchannel \( |\psi| \) tends to localize near values of \( R \) where \( C_\text{eff}(R) \sim C_{\text{eff}} \). Likewise, fragmentation channels are likely to be constructed and populated at values of \( R \) where a centrifugal component \( \Lambda_{\text{c}} \mid_{\text{eff}} \) diminishes in value, to be replaced by a rising value of \( C_{\text{eff}} \). Experience will be required to learn to map many-body physics in these terms. In the next section we give a preliminary illustration.

Already Ref. 13 had made a start in interpreting the eigenphases themselves. There it was stressed that eigenchannels \( |\psi| \) fall into three categories, depending on how the phases \( \phi \) rise with \( R \): (1) closed channels with small values of \( d^2\phi/dR^2 \), which are physically relevant only at higher energies; (2) “wide-open” channels with large values of \( d^2\phi/dR^2 \), which typically represent fully fragmenting channels such as ionization processes; (3) “interesting” channels with intermediate values of \( d^2\phi/dR^2 \). These last represent resonant channels that drift slowly toward large \( R \) because their energy is largely tied up in degrees of freedom transverse to \( R \). These are the channels in which energy is being shared among the constituents in an interesting way, and for which detailed study of the quantities \( \Lambda_{\text{c}} \mid_{\text{eff}} \) and \( C_{\text{eff}} \) should prove most illuminating.

Note, too, the formal structure of (13) and (15). Viewing \( \Lambda \) as a “time-like” coordinate that parameterizes the system’s evolution from compact to fragmented limits, the “time” evolution of the operators \( \Lambda \) and \( C \) is given by their commutators with the outward-bound Hamiltonian \( \tilde{H} \). That is, the centrifugal and Coulomb energies evolve in a way reminiscent of the Heisenberg equations of motion, further emphasizing their role in the system’s evolution from small to large \( R \).!

### 3 Initial Conditions

In the small-\( R \) limit solutions to the Schrödinger equation of hyperspherical harmonics, as noted above. Even though evolution equations have avoided explicit dependence on these harmonics, they are still needed to construct the initial Coulomb matrix \( C_{\text{Coul}}(R \to 0) = C_{\text{Coul}} \). Fortunately this problem is been well studied. The Coulomb matrix can be constructed by a direct approach or by exploiting the Lie group symmetries of the hypersphere. Since the actual hyperspherical harmonics and their matrix elements are disregarded for \( R > 0 \), a simpler alternative may be simply to diagonalize \( \Lambda \) and \( C \) in a suitable basis of Slater determinants at a fixed infinitesimal value of \( R \). The eigenphases themselves behave as \( \phi \to R(\lambda + (3N - 4)/2) \) as \( R \to 0 \) for the appropriate value of \( \lambda \).

#### 2.4 Behavior at Large \( R \)—The Miracle of the R-Matrix

In general the R-matrix serves as a set of short-range boundary conditions to which a set of asymptotic (large-\( R \)) wave-functions must be matched to satisfy physical boundary conditions. Since the phase-energy representation has discarded wave-functions, it seems that such a matching is no longer possible. However, much interesting collision physics focuses on resonances, particularly when the issue arises of how energy is shared between strongly interacting constituents. An elementary example is the energy sharing of the electron pair in the autoionizing resonances of helium. In such cases all that matters is that the calculation is continued to sufficiently large hyperradius \( R \) to contain the region of space within which the resonant state is confined. The resonant information is then already contained within the eigenchannels of the R-matrix, without the need to apply long-range boundary conditions.

We illustrate this principle using a two-channel example. Suppose channel 1 is open, and channel 2 is closed. Then, using the language of quantum defect theory, at large \( R \) two linearly independent solutions to the coupled-channel Schrödinger equation can always be written as the columns of a solution matrix

\[
F = \begin{pmatrix} f_1 & g_1 \end{pmatrix} \begin{pmatrix} f_2 & g_2 \end{pmatrix}
\]

in terms of regular and irregular reference functions \( f_i, g_i \) in each channel:

\[
\begin{align*}
 f_1 & \to \frac{1}{\sqrt{k_1}} \sin(k_1 R + \eta_1), \\
 g_1 & \to \frac{1}{\sqrt{k_1}} \cos(k_1 R + \eta_1), \\
 f_2 & \to \frac{1}{\sqrt{2k_2}} (\sin \beta \exp(k_2 R) - \cos \beta \exp(-k_2 R)), \\
 g_2 & \to \frac{1}{\sqrt{2k_2}} (\cos \beta \exp(k_2 R) + \sin \beta \exp(-k_2 R)),
\end{align*}
\]

as \( R \to \infty \). These solutions are normalized so that their
Wronskians \( f_i g_i' - g_i f_i' \) are both unity. If we were to eliminate the closed channel in the usual quantum defect theory sense we would find that the physical wave-function in channel 1 becomes

\[
\psi_{\text{op}} = -(\sin \beta + \cos \beta K_{22}) \left\{ f_1 - g_1 \left[ K_{11} - \frac{K_{12}^2}{\tan \beta + K_{22}} \right] \right\},
\]  

(19)

which identifies the quantity in square brackets as the resonant \((1 \times 1)\) K-matrix.

Now suppose we don’t eliminate closed channels, but just ask the R-matrix what it thinks is going on. The R-matrix, defined as

\[
\mathcal{R} = F(F')^{-1},
\]

(20)

is easily worked out in this two-channel case in terms of the general solution (16). In particular, its off-diagonal element is

\[
\mathcal{R}_{12} = \frac{K_{12}}{(-f_1' + g_1(K_{11})f_2' + [f_1K_{22} + g_1(K_{12}^2 - K_{11}K_{22})]g_2'}). 
\]

(21)

Since channel 2 is closed, either \( f_2' \) or \( g_2' \) (or more typically both) will diverge at large \( R \), i.e., when \( R \) is larger than the resonant state. Since the numerator of \( \mathcal{R}_{12} \) is constant, \( \mathcal{R}_{12} \) tends exponentially to zero as \( R \to \infty \). In other words, the R-matrix eigenchannels automatically segregate open and closed channels.

If this is the case, then the resonance should also appear in the open channel. The general form of the diagonal element in channel 1 is

\[
\mathcal{R}_{11} = \frac{(-f_1' + g_1(K_{11})f_2' + [f_1K_{22} + g_1(K_{12}^2 - K_{11}K_{22})]g_2')}{(-f_1' + g_1(K_{11})f_2' + [f_1K_{22} + g_1(K_{12}^2 - K_{11}K_{22})]g_2')}. 
\]

(22)

In the limit of large \( R \), \( f_2 = \sin \beta \exp (K_2 R) \) and \( g_2 = \cos \beta \exp (K_2 R) \) (assuming \( K_2 > 0 \)), whereby the R-matrix eigenvalue becomes

\[
(-f_1' + g_1K_{11}) \sin \beta - [f_1K_{22} + g_1(K_{12}^2 - K_{11}K_{22})] \cos \beta, \\
(-f_1' + g_1K_{11}) \sin \beta - [f_1K_{22} + g_1(K_{12}^2 - K_{11}K_{22})] \cos \beta.
\]

(23)

This last quantity clearly has the form \( \psi_{\text{op}}/\psi_{\text{op}} \) for some open-channel wave-function \( \psi_{\text{op}} \). This is of course appropriate if \( \mathcal{R}_{11} \) is the effective R-matrix in this channel. After a little rearrangement we find

\[
\psi_{\text{op}} = -(\sin \beta + \cos \beta K_{22}) \left\{ f_1 - g_1 \left[ K_{11} - \frac{K_{12}^2}{\tan \beta + K_{22}} \right] \right\},
\]

(24)

i.e., the same resonant wave-function as (19), apart from a normalization constant. This implies that R-matrix eigenchannels know all about resonant scattering, without ever invoking long-range boundary conditions.

The same general argument holds in a multichannel case. Indeed, Ref. 13 determined He\(^+\) autoionizing resonances in just this way, by following the energy dependence of eigenphases at a constant finite value of \( R \).

3. ILLUSTRATION: THE HELIUM ATOM RE-REVISITED

In this section we illustrate the merits of the phase-energy representation by applying it to the well-known problem of the autoionizing resonances of helium. Specifically, we restrict ourselves to the lowest-lying doubly excited states of \( ^1S^p \) symmetry. In the adiabatic representation these resonances are denoted \( x(K, T) \)\( = \) \( \sigma^+ (1, 0)^2 \) and \( \sigma^-(1, 0)^2 \). In this case, rather than use Jacobi coordinates, it is convenient to use the coordinates \( \vec{r}_1 \) of the two electrons referred to the nucleus, assumed fixed. In this case the relevant hyperspherical coordinates are defined by

\[
R = \sqrt{r_1^2 + r_2^2}, \quad \theta_{12} = \cos^{-1}(\vec{r}_1 \cdot \vec{r}_2), \quad \alpha = \tan^{-1}\left(\frac{r_2}{r_1}\right).
\]

(25)

Of course the derivation of the phase-energy equations (13)–(15) is the same in these coordinates as well.

The effective Coulomb function \( C(\alpha, \theta_{12}) \) is well known in these coordinates. We reproduce it in Fig. 1 for reference. In particular, there are three relevant angular regions that set the topography of this function: (1) For \( \alpha \to 0 \) or \( \to \pi/2 \), \( C \to -\infty \), establishing a potential valley corresponding to an ionization configuration. (2) For \( \alpha \to \pi/4 \) and \( \theta_{12} \to 0 \), \( C \to +\infty \), denoting the overlap of the two electrons. (3) For \( \alpha \to \pi/4, \theta_{12} \to \pi \), \( C \) experiences a saddle point known as the "Wannier ridge."

Solutions to the phase-energy equations are shown in Fig. 2. These solutions represent the direct integration of the equations, performed using a fifth-order Runge-Kutta method.\(^{(21)}\) For this illustrative calculation we have included an initial basis consisting of the hyperspherical harmonics \( \lambda = 0-6 \) in the \( R \to 0 \) limit. The results are thus not well converged, yet show the essential features.

Figure 2a shows the eigenphases \( \Phi_p(R) \) themselves. Similar eigenphases have been discussed extensively in Refs. 13 and 16. Briefly, the most rapidly rising phase represents the \( 1s\sigma \) ionization channel (this is a channel of the "wide-open" type referred to above). The most slowly growing phases represent closed channels that contain the seeds of higher-lying doubly excited states. Finally, the two eigen-
phases with intermediate values of $d\phi_p/dR$ are the "interesting" channels that stand for the doubly excited states. Their energy variation at large $R$ identifies the positions and widths of the resonances, as discussed in Ref. 13. Channel coupling tends to occur at ranges of $R$ where the eigenphases become nearly degenerate, as suggested by the denominator of (14). The strongest of these couplings lies at a hyperradius of $R = 3.5$ a.u., where the crossings are strongly avoided. It is here that the competition between centrifugal and Coulomb energies is won or lost.

Computing these channels in the phase-energy representation affords a fresh look at this competition. To see this, we plot in Figs. 2b and 2c the effective centrifugal term $\Lambda^2_{pp}(R)$ and the effective charge $C_{pp}(R)$ respectively. Only those channels corresponding to the ionization channel and the two resonant channels are shown, for clarity. The evolution of these quantities is smooth on the whole, although there are sharp features associated with the ambiguity in the channel labels $\rho$ in the regions of avoided crossings of the eigenphases.

Nevertheless, an essential feature of Figs. 2a and 2b is that between the avoided crossings these quantities are nearly constant. This fact indicates that the electron pair propagates for the most part guided by a set of independent eigenchannels with effective values of $\Lambda^2$ and $C$. The effective values are subsequently modified at each avoided crossing. This localization in $R$ of the significant channel interactions, which generalizes the avoided crossing of adiabatic potential energy curves, is an essential feature of the Fano view.\(^{(2)}\)

The transformation from centrifugal-dominated, independent-particle behavior at $R = 0$ to correlated behavior at larger $R$ is mapped by the variation of the quantities $\Lambda^2_{pp}(R)$ in Fig. 2b. These quantities are labeled by their centrifugal quantum numbers $\lambda$ in the $R \to 0$ limit. Their values do not change significantly until $R = 3.5$, the hyperradius of the primary avoided crossing. After this crossing their values are scrambled, indicating that the corresponding channels are far from the original hyperspherical harmonics. Interestingly, all three values coalesce near the same value, indicating an effective value $\lambda = 2$ of the centrifugal quantum number.

Clues hinting at what these channels become after they are rearranged are provided by the evolution of the effective charge $C_{pp}(R)$ in Fig. 2c. The charge begins to vary almost immediately, since it is not diagonal in the $R \to 0$ limit. Indeed, after the first crossing two channels have mixed to yield $C_{pp} = -7$. The corresponding contour on the $C(\alpha, \theta_{12})$ plot in Fig. 1 suggests that these channels are beginning to fall into the valley, i.e., tending toward single ionization. The influence of the major avoided crossing at $R = 3.5$ a.u.

Figure 1. Contour plot in atomic units of the effective charge function $C(\alpha, \theta_{12})$. Contours are equally spaced at 1 a.u. intervals.

Figure 2. A doubly excited helium resonance as viewed in the phase-energy representation. (a) A set of eigenphases (modulo $\pi$) as in Ref. 13. (b) The effective centrifugal energies $\Lambda^2_{pp}$ of the three channels whose eigenphases rise most rapidly in (a). These are labeled by the index $\lambda$ of the hyperspherical harmonic to which they reduce in the $R = 0$ limit. (c) The effective charge $C_{pp}$ in each of the three channels shown in (b). Notice that $\Lambda^2_{pp}$ and $C_{pp}$ can suddenly change their values whenever the phases in (a) experience avoided crossings.
changes this picture, however. At this crossing, the channels are rearranged so as to plunge the ionization channel much deeper into the valley, with $C_{oo} = -9$. Correspondingly the effective charge in the pushed channel is raised to a higher value, $C_{pp} = -5$.

The channel rearrangement thus affords a glimpse of the physics of electron correlations in this case. Namely, once one channel decisively enters into the potential valley, it forces the other channels to settle at higher potential energies, since all the channels must remain orthogonal. Interestingly, the effective charge $C_{oo} = -5$ in the resonant channel nearly coincides with the value of $C(e, \theta_{12})$ on the Wannier ridge. Since $C_{pp}$ represents the mean value of $C(e, \theta_{12})$ in the channel $p$, it follows that the electron pair in this channel must spend at least part of its time near the ridge configuration. Note that this remark by itself does not speak to the long-standing debate on whether the electrons really are localized there\(^{(22)}\) or whether they just dwell there on their way through.\(^{(23)}\) Nevertheless, the quantum-mechanical branching of the channels is well documented in this picture.

4. OUTLOOK

If many-body Coulomb dynamics is a competition, then Fig. 2 is the scorecard. Namely, in each eigenchannel $p$ we can keep track separately of the partition of the total energy $E$ into its (outbound) kinetic, centrifugal, and potential components. In this compact “phase-energy” form we no longer need to consider explicitly every degree of freedom of the $N$-body problem, which should enable the extension of hyperspherical methods to ever more elaborate systems. Nevertheless, many examples need to be worked out before we fully understand how to read the scorecard.

In addition, the phase-energy form of the Schrödinger equation ought to lend itself to a suitable numerical procedure. So far its accuracy is still limited by the size of the initial hyperspherical harmonic basis set employed at $R = 0$. Future work should adapt numerics to the eigenchannel-following philosophy of the method, and include only those eigenchannels that are relevant in a given energy range. This procedure would bring us one notch closer to realizing Fano’s unified vision of atomic physics.

Acknowledgments

This work was supported by the National Science Foundation. I gratefully acknowledge C. Greene for pointing me toward the quantum defect analysis of the $R$-matrix at large $R$. More significantly, I thank U. Fano for sharing his vision on this and many other subjects.

Received 13 May 2000.

Résumé

Dans le cadre de la mécanique quantique, le problème à plusieurs corps interagissant via la force coulombienne est exactement formulé dans une représentation “phase-énergie”. Au lieu de chercher une fonction d’onde de plusieurs corps, cette approche détermine un groupe de phases caractéristiques qui décrit l’évolution d’un système entre ses limites et compactes et de fragmentation. Les phases caractéristiques dépendent des valeurs des énergies cinétiques et potentielles pendant l’évolution du système. Une illustration des résonances de l’hélium montre que l’information concernant la nature des canaux caractéristiques est codée dans ces énergies.

Personal Note

\(^{1}\) Back in our Chicago days Emil Sidky and I used to joke that we would cast the U.S. economy in hyperspherical coordinates and make ourselves rich. I defer this task to a future paper.

References


John L. Bohn
JILA, University of Colorado and National Institute
of Standards and Technology
Boulder, Colorado 80309-0440 U.S.A.

e-mail: bohn@murphy.colorado.edu