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# Channel-interaction theory in a finite volume

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The power and scope of configuration-interaction studies can be greatly extended by limiting the variational calculation to a finite volume of configuration space. The energy levels and wave functions of an electron which escapes from that volume are then accurately described by quantum-defect theory. Adaptation of standard multiconfiguration Hartree-Fock procedures to the variational calculation of $R$ matrices is accomplished easily, giving a simple, fast, and efficient tool for investigating channel-coupling mechanisms over broad ranges of energy.

Recently a new eigenchannel formulation of $R$-matrix theory was developed to treat atomic photoionization in the presence of a magnetic field.[1] Presented as a tentative alternative to a method developed by Fano and Lee,[2] it simplified and streamlined their approach while retaining its main insight—the strong dominance of a few scattering eigenmodes in many problems.[3] Since the limited application of Ref. 1 was published, the approach has been extended to study doubly excited $P$ and $D$ states of Be, Mg, and Al,[4-6] giving an excellent description of the atomic dynamics and with unexpected ease. A parallel development in molecular physics[7] has produced reliable data on some doubly excited ungerade states of $H_2$.[8]

The small scale of the numerical efforts required to perform such calculations and the ease of extracting correlated wave functions for analysis and dissection suggest that we are now on the verge of being able to unravel coupling mechanisms governing atomic spectra throughout the periodic system. This development has implications far beyond an improved technical ability to calculate energy levels for comparison with experiment. Rather, the main progress seems to lie in an improved facility for detailing the evolution of electron correlations over broad ranges of energy (typically $\gtrsim 10$ eV) and for different atoms in a column of the periodic system. O'Mahony[6] has quite recently shown how a similar orbital hybridization governs $sd$-$p^2$ mixing in Mg and Al, indicating that the analysis lends itself to a study of trends across a *row* of the periodic system without much additional complexity. This study offers a glimpse into the nature of channel coupling which should have relevance to even heavier systems such as the transition metals.

The canonical method for studying atomic spectra starts from an independent electron model. The Hartree-Slater treatment represents its simplest form: each electron is presumed to move in the same local potential due to the nucleus and the other electrons.[9] The somewhat more realistic Hartree-Fock approach[10] allows for a nonlocal electronic potential operator. These formulations can only provide an accurate quantitative description of a single electron outside a closed-shell core, but represent nevertheless many physical properties of atoms, such as sizes, ionization potentials, and potential barrier effects[11] correctly on a qualitative and semiquantitative level. A superposition of these independent electron configurations, determined variationally as in the multiconfiguration Hartree-Fock (MCHF) approach,[10] gives a solid quantitative description of perturbed, low-lying atomic spectra.

On the other hand, the classification of channel coupling mechanisms can be aided by plots of potential-energy curves in hyperspherical coordinates.[5,6,12] These plots identify the regions in configuration space and in energy where inelasticity originates. They also permit a rapid estimation of channel coupling strength, even though the hyperspherical formulation has not achieved state-of-the-art accuracy for the quantitative calculation of autoionization profiles, discrete level perturbations, or other related properties.

The motion of interacting electrons is generally complicated by correlations and exchange only within a small reaction volume $\Omega$ of configuration space. This important dynamical simplification is not effectively utilized by the MCHF approach. $R$-matrix theories can exploit it by solving the full, many-electron Schrödinger equation within this reaction volume only (but past procedures have often led to overextended volumes).[13-16] Escape of a single electron beyond this volume is then described accurately by quantum-defect theory.[17,18] That is, the electron wave function and its normal derivative are matched on the reaction surface $\Sigma$ to a channel expansion with regular and irregular radial solutions $(f_i,g_i)$ in each channel $i$. (See Ref. 4 for details.) The reaction-matrix eigenvalues $\tan(\pi\mu_\alpha)$ and eigenvectors $U_{i\alpha}$ thus obtained vary quite slowly with the energy. These parameters are, accordingly, the best suited for studying the interesting *short-range physics* in successive atoms as a function of energy. The point-by-point calculation of scattering or photoabsorption cross sections requires instead a much finer energy mesh, but it involves very little time since it is handled by algebraic quantum-defect procedures.

The version of $R$-matrix theory used most widely in atomic and molecular problems[13] diagonalizes the small-$r$ Hamiltonian $H$ in an orthonormal basis of functions $y_k$ having a common normal logarithmic derivative $(-b^0)$ on the surface $\Sigma$ of the reaction volume:

$$\frac{\partial y_k}{\partial n}+b^0 y_k=0,\ \text{on surface }\Sigma\ . \tag{1}$$

Because the exact wave function at an arbitrary energy $E$ does not itself satisfy (1), however, the expansion of the logarithmic derivative using the basis set $y_k$ does not converge uniformly. This extremely slow convergence can be speeded up somewhat using the Buttle correction[19] or a variational correction,[20] but it remains a difficulty of the approach. A second version of the $R$-matrix theory used less extensively to date, the eigenchannel method, has been applied to nuclear problems by Danos and Greiner[21] and to atomic problems by Lee and Fano.[2] This version diagonalizes $H$ using basis functions $y_k$ having the *same* logarithmic derivative on the reaction surface as the exact wave function $\psi$:

$$\frac{\partial y_k}{\partial n}+by_k=0,\quad \frac{\partial\psi}{\partial n}+b\psi=0,\ \text{on surface } \Sigma\ . \tag{2}$$

This expansion converges uniformly, but since $b$ is not known in advance the Hamiltonian must be diagonalized iteratively as a function of $b$ until one of the resulting energy eigenvalues $E_\beta$ coincides with the desired total energy $E$. Iterative diagonalization can be time consuming and inconvenient, and therefore much of the appeal of the $R$-matrix method is lost in the eigenchannel version, in contrast with the approach of Ref. 13, which requires only one diagonalization to determine $b_\beta$ at all energies.

The point of the noniterative reformulation of the eigenchannel $R$-matrix method used in Refs. 1 and 4–8 is to show how the eigenvalues $b_\beta$ of the $R$ matrix can be determined without iteration, using a single diagonalization for each desired energy $E$. The variational basis functions $y_k$ need not have any particular logarithmic derivative $b_k^0$ on the boundary; in fact, the $b_k^0$ should ideally span a range of values. Moreover, the $y_k$ need not be orthogonal, allowing great flexibility in their choice. This approach is similar in spirit to the variational formulation of $R$-matrix theory used by Lane and Robson[22] and applied by Purcell,[23] Chatwin,[24] Oberoi and Nesbet,[25] and Nesbet,[26] also using nonorthogonal bases. It is a close relative of the Kohn variational principle.[27,28] In contrast with Refs. 22–26, though, the present approach does not involve the inversion of a nearly singular matrix, which caused some numerical difficulties in applications.

As derived in Ref. 1, the noniterative eigenchannel treatment rests on a variational principle for an eigenvalue $b$ of the $R$ matrix:

$$b=\frac{\int_\Omega[-\nabla\psi^*\cdot\nabla\psi+2\psi^*(E-V)\psi]\,d\omega}{\int_\Sigma\psi^*\psi\,d\sigma}\ . \tag{3}$$

In this stationary expression for $b$, $d\omega$ is the differential volume element of configuration space and the integrals extend only over the reaction volume $\Omega$. The denominator is an integral over the surface $\Sigma$ of the reaction volume, whose differential area element is denoted $d\sigma$. In the numerator $V$ indicates the total potential energy of the system and $\nabla$ represents a $3N$-dimensional gradient operator for the $N$-electron system. It is important to recognize that no constraint needs to be imposed on the trial functions in showing that (3) is variational, that is, that $\delta b=0$. In particular, the trial functions need not have any specified logarithmic derivative on the reaction surface $\Sigma$. [Equation (3) is easily obtained using the general approach of Gerjuoy, Rau, and Spruch,[29] as detailed by Raseev.[8]]

The variational principle (3) is usually reduced to a homogeneous linear system by introducing a set of basis functions $y_k$ in the expression

$$\psi=\sum_k c_k y_k\ . \tag{4}$$

The stationary values of $b$ in Eq. (3) are then the eigenvalues of a generalized eigenvalue problem,

$$\underline{\Gamma}\mathbf{c}=b\underline{\Lambda}\mathbf{c}\ , \tag{5}$$

where the Hermitian matrices $\underline{\Gamma}$ and $\underline{\Lambda}$ are defined by

$$\begin{aligned}\Gamma_{kl}&=\int_\Omega[-\nabla y_k^*\cdot\nabla y_l+2y_k^*(E-V)y_l]\,d\omega\\&=2\int_\Omega y_k^*(E-H)y_l\,d\omega-\int_\Sigma y_k^*(\partial y_l/\partial n)\,d\sigma\end{aligned} \tag{6}$$

and

$$\Lambda_{kl}=\int_\Sigma y_k^* y_l\,d\sigma\ . \tag{7}$$

The second form in Eq. (6) is usually more convenient, in terms of a non-Hermitian Hamiltonian matrix element and of a surface term which makes $\underline{\Gamma}$ Hermitian. Each eigenvalue $b_\beta$ corresponds to an eigenmode of the short-range Hamiltonian, whose wave function is easily reconstructed from the associated eigenvector. Graphs of these eigenmodes often point immediately to the dominant mechanisms of channel coupling.[4]

In applications to atomic dynamics, a "Cartesian" reaction surface $\Sigma$, defined by

$$\max(r_1,r_2,\ \dots\ )=r_0\ , \tag{8}$$

is most convenient for matching onto asymptotic channel states representing one-electron escape. Moreover the general success of the independent-electron model suggests that the basis functions $y_k$ be represented as Slater determinantal wave functions, e.g., for two electrons,

$$y_{n_1n_2}(\mathbf{r}_1,\mathbf{r}_2)=\mathcal{A}\phi_{n_1}(\mathbf{r}_1)F_{n_2}(\mathbf{r}_2)\ . \tag{9}$$

In Eq. (9), $\mathcal{A}$ denotes antisymmetrization and $\phi_{n_1}(\mathbf{r}_1)$ is a wave function of the $(N\text{-}1)$-electron system which vanishes at $r_1=r_0$. Instead, the orbital $F_{n_2}(\mathbf{r}_2)$ has been chosen in Refs. 4–6 to be a numerical, independent-electron orbital of the $N$-electron system. That is, $F_{n_2}(\mathbf{r}_2)$ is an eigenstate of a *different* one-electron Hamiltonian than $\phi_{n_1}(\mathbf{r}_1)$, and accordingly is not orthogonal to the $\phi_{n_1}$, unless their angular wave functions differ. Moreover, the $F_{n_2}(\mathbf{r}_2)$ do not all vanish at $r_2=r_0$ (except for strongly closed channels), and their logarithmic derivatives span a range of values.

These numerical trial wave functions $y_k$ are generally the *same* for a fairly large range of energies, up to a sizable fraction of one atomic energy unit. The most time-consuming part of the calculation, the numerical evaluation of $1/r_{ij}$ matrix elements, needs then to be performed only once. The rapid convergence of these finite-volume basis expansions enables even multiple excited states to be handled with surprisingly small-scale calculations. Basis sets consisting of 20 to 30 $(y_k)$ were used in Refs. 4–6, and tests showed them to be accurately converged. The entire calculation for a given symmetry of an atom, including construction of numerical basis functions and matrix elements, solution of the eigensystem (5), matching to Coulomb wave functions at the reaction surface, and the use of quantum-defect theory to find energy levels and oscillator strengths, required somewhat less than 10 min of CPU (central processing unit) time on a Digital Equipment Corporation VAX11/780 computer or RIDGE 32 computer for Be, for Mg, and even for Al. Moreover, the computer code implementation is sufficiently simple that development of a large general problem seems unnecessary.

O'Mahony's results for Al $^2D^e$ quantum defects below and above the ionization threshold are shown in Fig. 1.[6] In this problem the $3s^2nd$ Rydberg levels converging to the lowest level of $\mathrm{Al}^+(3s^2\,{}^1S)$ interact strongly with a perturber $3s3p^2$ which is distributed along the entire series of $3s^2nd$ Rydberg levels and even into the $3s^2\epsilon d$ continuum. Its presence is signaled by the slow rise of $\mu$ by roughly unity in Fig. 1 as the energy increases from $-0.1$ to 0.05 Ry. The experimental quantum defects[30] marked on the figure clearly reflect this energy dependence, agreeing nicely with the calculation except for an overall shift of about 0.05, which is probably related to the use of a too-simple model potential (Hartree-Slater) to represent the $e^-$-$\mathrm{Al}^{3+}$ interaction. Figure 1 illustrates a common example of strong, nonperturbative channel interactions which would be difficult to describe by MCHF programs treating all of configuration space at once. The channel mixing poses no particular difficulty, however, if the configuration-interaction calculation is limited to a finite volume, e.g., $r_0 = 11$ a.u. for Al $^2D^e$ states in the energy range of Fig. 1.

This program of study now appears ripe for investigating more complicated open-shell systems. Its aim is not just to determine energy levels and oscillator strengths, but also to identify major trends in the few-electron dynamics which extend across rows and down columns of the periodic table. Initial indications are that nonperturbative multiphoton interactions with whole subshells of atomic electrons will also be accessible to this type of formulation, since the strong coupling still remains confined within a compact volume.[31]

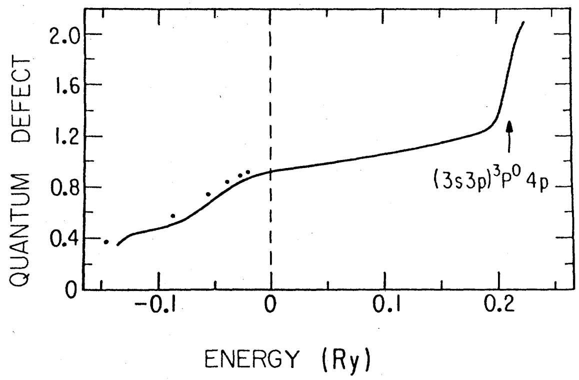

FIG. 1. O'Mahony's (Ref. 6) calculated quantum defect for the $3s^2\epsilon d$ channel of Al is shown as a function of the energy relative to the ionization threshold. The experimental quantum defects (Ref. 30) of six levels below threshold are also shown for comparison.

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