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Variational Calculation of R Matrices. Application to Ar Photoabsorption*

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An *ab initio* analytic Hartree-Fock procedure is introduced which yields directly eigenvalues and eigenvectors of an R matrix to be matched with data extracted from different spectroscopic experiments. Results of a pilot calculation are presented.

The net effect of complicated short-range interactions between one particle and a compact aggregate can be summarized by the boundary values of the particle's wave function on a surface S that envelops the aggregate. The effect of additional long-range forces can then be worked out by solving the Schrödinger equation for the single particle's motion outside S . This concept was embodied in Wigner's proposal that many-body theories of nuclear scattering should aim at calculating an R matrix.¹ In atomic and molecular problems the long-range forces are predominantly central and Coulombic when the "aggregate" is a positive ion; they are then treated analytically by the quantum-defect theory (QDT).² (Non-Coulomb forces require further work but are disregarded here.)

Use of the R matrix in atomic problems by QDT permits (a) *joint* treatment of bound Rydberg states of an excited electron and of its unbound scattering states, and (b) *interpolation* between energy levels, transition probabilities, and scattering amplitudes of all these different states insofar as the R matrix depends weakly on the total energy of the system. This interpolation property has been exploited extensively by our group as a device for unified representation of very diverse experimental data in terms of *eigenvalues* and *eigenvectors* of an R -type matrix.³ Each

eigenvector Ψ_α can be viewed as a particular superposition of ion plus electron states with alternative angular momenta and couplings, largely independent of the degree of excitation. Accordingly, it identifies a whole channel of excitation rather than individual levels; attention has been directed to "eigenchannels" in nuclear physics too.⁴ The eigenvalues are expressed conveniently as quantum defects μ_α , even though they are seldom observed directly in this form. These eigenvalues and eigenvectors serve well as interface for comparing *ab initio* theory with experimental evidence because they constitute a *minimal but complete set* of spectroscopic and scattering data.

Ab initio calculations of R matrices have been scarce. The traditional analytical approach utilizes a set of eigenfunctions whose truncation suffers from notoriously slow convergence. This difficulty, experienced in recent atomic applications,^{5,6} has stimulated the search for alternative approaches in the present work and in independent model studies.^{7,8} We outline here an approach that yields the R matrix directly in its diagonal, physically significant form, and we compare the results of a pilot calculation to experimental evidence.

Consider, for simplicity, the variational expression for stationary states of a single particle

within a sphere of radius r_0 ,

$$\delta \int_{r \leq r_0} \psi^*(\vec{r}) [-\frac{1}{2} \nabla^2 + U(\vec{r}) - E] \psi(\vec{r}) d^3 r = 0, \quad (1)$$

where $U(\vec{r})$ is an arbitrary self-adjoint potential operator. Integration by parts changes Eq. (1) into

$$\delta (-\frac{1}{2} r_0^2 \int_{4\pi} [\psi^*(\vec{r}) \partial \psi / \partial r]_{r=r_0} d\Omega + \int_{r \leq r_0} \{ \frac{1}{2} |\nabla \psi(\vec{r})|^2 + [U(\vec{r}) - E] |\psi(\vec{r})|^2 \} d^3 r) = 0. \quad (2)$$

We incorporate the surface term formally into the volume integral by a δ -function notation, rewriting Eq. (2) as

$$\delta \int_{r \leq r_0+} \{ \frac{1}{2} |\nabla \psi(\vec{r})|^2 - \frac{1}{2} \delta(r - r_0) \psi^*(\vec{r}) \partial \psi / \partial r + [U(\vec{r}) - E] |\psi(\vec{r})|^2 \} d^3 r = 0, \quad (2a)$$

where the limit r_0+ specifies that the integration includes the singularity of the δ function.

This variational problem over the finite spherical volume yields a discrete set of energy eigenvalues when complemented by a boundary condition at $r = r_0$. Familiar boundary conditions are $\psi(r_0) = 0$ for a reflecting wall and $(\partial \psi / \partial r)_{r=r_0} = 0$, the "zero momentum" condition; both are special cases of the homogeneous condition

$$[\partial \psi / \partial r + b \psi(r)]_{r=r_0} = 0, \quad (3)$$

which assigns a value b of the normal logarithmic derivative. We regard b as a constant parameter, unless otherwise stated, but an arbitrary real function $b(\hat{r})$ of the position \vec{r} on the boundary would be acceptable. Substitution of (3) reduces Eq. (2a) to the form

$$\delta \int_{r \leq r_0+} \{ \frac{1}{2} |\nabla \psi(\vec{r})|^2 + [\frac{1}{2} b \delta(r - r_0) + U(\vec{r}) - E] |\psi(\vec{r})|^2 \} = 0. \quad (4)$$

The traditional procedure for calculating an R matrix may start from this equation, assuming an arbitrary value of b and calculating the spectrum of energy eigenvalues and eigenfunctions.

Here we stress, instead, the symmetry of Eq. (4) with respect to interchange of b and E . Each of them enters (4) as the coefficient of a volume integral of $|\psi(\vec{r})|^2$ multiplied by a non-negative weight function, which is $\frac{1}{2} \delta(r - r_0)$ for b and unity for E . (We are indebted to F. Calogero for this remark.) Therefore we may use the variational equation (4) to determine a complete set of eigenvalues b_α and eigenfunctions Ψ_α , for any fixed value of the energy E , instead of determining a complete set of E_λ and Ψ_λ for any fixed b . The set of Ψ_α is orthogonal and complete over the weight function $\frac{1}{2} \delta(r - r_0)$, i.e., in effect over the boundary $r = r_0$. Hence the calculation of a scattering or bound-state wave function of the particle in the outer region, $r \geq r_0$, can start from boundary values expanded in the form $\psi(\vec{r}_0) = \sum_\alpha c_\alpha \Psi_\alpha(\vec{r}_0)$, $(\partial \psi / \partial r)_{r_0} = -\sum_\alpha c_\alpha b_\alpha \Psi_\alpha(\vec{r}_0)$. In this expansion the b_α and $\Psi_\alpha(\vec{r}_0)$ play the role of eigenvalues and eigenvectors of the "logarithmic derivative," or R , matrix. Scattering states are degenerate, with the expansion coefficients c_α depending on boundary conditions at $r = \infty$; bound states are identified by $\psi(\infty) = 0$ and exist only for discrete values of E . (The simple example of a single particle in a central potential yields a single eigenvalue b_α for each angular momentum.)

The eigenvalue problem for b has the following mechanical interpretation. The term $\frac{1}{2} b \delta(r - r_0)$ in Eq. (4) may be regarded as representing a mock potential barrier (or "moat" when $b < 0$) whose effect increases $\partial \psi / \partial r$ discontinuously from a value $-b\psi$ at $r = r_0-$, i.e., just inside the barrier, to the value zero at $r = r_0+$. That is, b identifies the height of the mock barrier required for the Schrödinger equation to be solvable with given energy E and with zero-momentum boundary condition at r_0+ . The required height is b/ξ , with $\xi > 0$, for a thin square-well barrier,

$$\delta(r - r_0) \xrightarrow{\xi \rightarrow 0} \begin{cases} 0 & \text{for } r < r_0 - \xi \\ 1/\xi & \text{for } r_0 - \xi \leq r \leq r_0. \end{cases} \quad (5)$$

In this representation the eigenvalue problem consists of determining the mock-barrier height for fixed E and fixed (mock zero momentum) boundary condition.

The applicability of this point of view is amplified by the remark that Eq. (4) is readily transcribed for an n -particle system enclosed in an arbitrarily connected region of its configuration space. We regard now $\vec{r} \equiv \{\vec{r}_1, \vec{r}_2, \dots, \vec{r}_n\}$ as a vector of this space and define the volume of integration as the locus

of positive values of a function $S(\vec{r})$, enclosed by the surface $S(\vec{r})=0$. Equation (4) takes the form

$$\delta \int_{S=0} \left\{ \frac{1}{2} |\nabla \psi(\vec{r})|^2 + \left[\frac{1}{2} b \delta(S) + U(\vec{r}) - E \right] |\psi(\vec{r})|^2 \right\} d^3r = 0, \quad (6)$$

to which the preceding discussion applies as well. This remark opens the way to direct calculation of eigenchannel properties utilizing the variational approach to *finite-volume many-particle* Schrödinger problems to any desired degree of refinement.

One of us (C.M.L.) has utilized Eq. (6) for calculating essential properties of the set of odd-parity, $J=1$, bound and ionized states of Ar atoms with energies up to ~ 20 eV above the ground state. The results are given here with details to follow elsewhere. These states are regarded as combinations of an Ar^+ ion, in either level of its doublet ground state ${}^2P_{3/2,1/2}$, and of an electron in an s or d orbital. Alternative combinations, inclusive of spin, yield five distinct channels:

$$i = \left. \begin{array}{ccccc} 1 & 2 & 3 & 4 & 5 \\ P_{1/2}d_{3/2} & P_{3/2}d_{5/2} & P_{3/2}d_{3/2} & P_{1/2}s_{1/2} & P_{3/2}s_{1/2} \end{array} \right\} J^\pi = 1^-. \quad (7)$$

Quantum-defect analysis of experimental data for this system⁹ has led to the quantitative characterization of five eigenchannels, $\alpha = 1, \dots, 5$, as superpositions of the channels i defined by Eq. (7). The properties of these eigenchannels have now been calculated *ab initio* in a Hartree-Fock approximation for comparison with the data obtained in Ref. 9.

Wave functions for continuum eigenchannel states of energy E are represented schematically by

$$\Psi_\alpha = \mathcal{Q} \sum_i \Phi_i F_{i\alpha}(r), \quad (8)$$

where \mathcal{Q} indicates antisymmetrization, Φ_i consists of Hartree-Fock wave functions of Ar^+ ¹⁰ combined with the angular and spin parts of the excited-electron's wave function in accordance with (7), and $F_{i\alpha}$ is a radial function for this electron, which remains to be determined by our variational approach. Bound-state wave functions are superpositions of Ψ_α which converge at $r \rightarrow \infty$ only for discrete energy eigenvalues E , but whose essential parts—at $r \leq r_0$ —are calculated for arbitrary E just as for the continuum. At radial distances exceeding a limit $r_0 \sim 5-10$ a.u., the QDT provides the analytical form^{2,3,9}

$$F_{i\alpha}(r) = U_{i\alpha} [f_i(r) \cos(\pi \mu_\alpha) - g_i(r) \sin(\pi \mu_\alpha)] \text{ for } r \geq r_0. \quad (9)$$

Here f_i and g_i are regular and irregular Coulomb wave functions for electron energy $E - E_i$, E_i being the Ar^+ energy level in the i th channel; the $U_{i\alpha}$ are elements of a 5×5 orthogonal matrix. Both μ_α and $U_{i\alpha}$ remain to be determined.

The expression (9) of $F_{i\alpha}$ for $r \geq r_0$ implies that Ψ_α satisfies the boundary condition (3) with a parameter $b(\mu_\alpha, E - E_i)$ which depends not only on μ_α but also on the energy $E - E_i$ of the electron at large r . In adopting a different value of b for different channels *we depart*, but only in detail, from our earlier development. For $r \leq r_0$, $F_{i\alpha}(r)$ was represented as the superposition of Slater base functions v_{ni} ,

$$F_{i\alpha}(r) = \sum_n c_{ni\alpha} v_{ni}(r), \quad (10)$$

with coefficients restricted by the boundary condition (3), with the appropriate b , and by normalization. Substitution of (8) and (10) into (6) yields a system of linear homogeneous equations in the coefficients $c_{ni\alpha}$ and $U_{i\alpha}$ with parameters μ_α and E . The integrations over \vec{r} , involving quadratically the products $\Phi_i v_{ni}(r)$, were done by standard numerical procedures. To optimize the variational fit over the whole volume, rather than on its

surface only, the system was solved first with trial μ_α 's to obtain eigenvalues E_λ and eigenvectors $(c_{ni\alpha}^{(\lambda)}, U_{i\alpha}^{(\lambda)})$. The value of μ_α was then varied iteratively to bring each of five E_λ , in

TABLE I. Ar ($J^\pi = 1^-$) parameters at the ${}^2P_{3/2}$ threshold, $E = E_0$.

Quantum defects $\mu_\alpha = \mu_{\alpha 0} + \mu_{\alpha 0}'(E - E_0)$, and dipole elements, D_α .					
(Experimental values in parentheses, from ref. 9.)					
α	1	2	3	4	5
$\mu_{\alpha 0}$.19(.22)	.01(.07)	.51(.50)	.12(.15)	.07(.11)
$\mu_{\alpha 0}'$ (eV ⁻¹)	.08(.05)	.00(.02)	.04(.07)	-.01(-.01)	-.01(-.02)
D_α (a.u.)	.05(.05)	-2.1(-2.1)	-.01(.12)	-.03(.00)	1.0 (1.4)
Transformation matrix $U_{i\alpha}$.					
Calc.					
	.70	.59	.59	.08	.01
	-.34	.77	-.54	-.10	.01
	-.63	.25	.72	.13	.01
	.00	.00	-.15	.81	-.56
	.00	-.01	-.10	.55	.83
Ref. 9					
	.70	.60	.38	.00	.01
	-.32	.75	-.58	.00	-.02
	-.64	.28	.72	.00	.02
	.00	.00	.02	.82	-.58
	.00	.00	-.02	.58	.82

turn, to coincide with a desired value of E . The entire operation requires ~ 260 sec on an IBM 370/168, for three values of E .

The resulting values of μ_α and $U_{i\alpha}$ are shown in Table I, together with the matrix elements for dipole excitation from the Hartree-Fock ground state,

$$D_\alpha = \int_{r_j \leq r_0} \Psi_\alpha^* \left(\sum_{j=1}^{18} z_j \right) \Psi_0 \prod_{j=1}^{18} d^3r_j, \quad (11)$$

and with the experimental values of the same parameters from Ref. 9. The differences of calculated and experimental values are not surprising in view of the inaccuracy of fitting in Ref. 9, and of the known importance of electron correlations—neglected here—for the excitation of Ar. The $U_{i\alpha}$ show the eigenchannels $\alpha = 1, 2, 3$ to consist mostly of d orbitals with LS coupling ($^3D, ^1P, ^3P$, respectively), while $\alpha = 4, 5$ correspond to s orbitals with 3P and 1P coupling; the D_α values are accordingly large for singlet-singlet transitions only.

Calculation of the R matrix by the alternative methods of Refs. 7 or 8, followed by its diagonal-

ization, should yield equivalent results.

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Hydrogenic Stark-Zeeman Spectra for Combined Static and Dynamic Fields

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The entire spectrum of hydrogen in combined static and periodic electric and magnetic fields is derived by using $O(4)$ algebra, and related to the corresponding simpler Lyman- α spectrum by a scaling relation. This time-dependent generalization of the Stark-Zeeman effects provides the necessary basis for the proper analysis of hydrogenic spectra for plasma diagnostic purposes.

In this Letter we provide a full description of the characteristics of the entire hydrogen spectrum under the influence of timewise periodic, but otherwise arbitrary, electric and magnetic fields. Within the framework of certain physical approximations, valid over a wide range of parameters, these results constitute a nonperturbative exact solution to the problem, based on Lie-algebraic methods, and thus remain valid for many physically interesting situations, including resonance domains,^{1,2} where perturbation

methods fail. One of the important areas where the knowledge of such spectra is required is plasma diagnostics by hydrogen spectroscopy, where the atoms are under the influence of combined time-dependent and quasistatic electric fields. Such situations arise both in laboratory plasmas^{3,4} and astrophysical plasmas (solar flares).⁵

The Blokhintsev⁶ theory describes the effect of simple dynamic electric fields; its inadequacy when both static (or quasistatic) and dynamic fields act simultaneously was pointed out by us