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Stark effect of nonhydrogenic Rydberg spectra

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Rydberg states of an atom in an electric field are represented in terms of hydrogen eigenfunctions for the same field but scattered by the ionic core of the actual atom. The effect of the Stark field on photoabsorption is expressed in terms of scattering and frame-transformation parameters.

Rau has singled out a set of diverse phenomena characterized by a wave function that extends over two regions of space, where fields of different symmetry prevail.[1] The Stark effect of Rydberg spectra, which exhibits remarkable features,[2] affords a prototype example amenable to complete treatment. The Rydberg electron's motion separates in parabolic coordinates in the Coulomb plus Stark field at large distances from an atom, but in polar coordinates near or within the atomic core where the Stark field is usually negligible.

Representing Rydberg states in terms of (a) hydrogenic wave functions at large distances, and (b) scattering of these wave functions by the ionic core of an atom (or molecule) is the trademark of the quantum-defect method (QDT).[3] Parameters of aspects (a) and (b) of a state are calculated separately and then combined analytically; the combination often involves a frame transformation, e.g., when *jj* and *LS* coupling are used in (a) and (b), respectively. This approach looks well suited to treating the Stark effect.[4] To this end it presupposes a full development of Stark-field wave functions for H (Ref. 5) and their adaptation to QDT,[6] which are now in hand. The necessary scattering parameters are common to other QDT applications. Combining these two sets of parameters requires a transformation from the frame of parabolic quantum numbers to the angular momentum frame which is normal for core interactions. This Communication shows how existing transformation formulas can in fact be extended, as required by the Stark problem, within a *limited region* of space. Thus it introduces the concept of a *local frame transformation,* which seems relevant to the treatment of any localized interaction.

The treatment developed here disregards quantities of order Fr_0 a.u., where the field strength $F=O(10^{-5}$ a.u.) in current experiments and the ionic radius $r_0=O(1$ a.u.).

A complete set of electron eigenfunctions for the Coulomb plus Stark potential, $-e^2/r+eFz$, with $(e,F)>0$, is represented by[5-7]

$$\psi_{nm}(F,\epsilon;\xi,\eta,\phi)=N_{n\epsilon}u_{1m}(F,\epsilon,\beta_n;\xi)\times u_{2m}(F,\epsilon,1-\beta_n;\eta)\times e^{\pm im\phi}(2\pi)^{-1/2}\ , \tag{1}$$

where $-\infty<\epsilon<\infty$ is the energy, $\xi=r+z=r(1+\cos\theta)$, $\eta=r(1-\cos\theta)$, $n=0,1,\ldots,$ is the number of nodes of u_{1m}, and $m\geq 0$. (The number n is indicated by n_1 in Refs. 5–7.) The functions u_{1m} and u_{2m} are Coulombic for $(\xi,\eta)\leq O(1)$ (in atomic units), are regular and normalized to $\xi^{m/2}$ or $\eta^{m/2}$ as $(\xi,\eta)\rightarrow 0$, and are renormalized by $N_{n\epsilon}$ to ensure the completeness

$$\tfrac{1}{4}(\xi+\eta)2\pi\sum_n\int_{-\infty}^{\infty}d\epsilon\,\psi^*_{nm}(F,\epsilon;\xi',\eta',\phi)\psi_{nm}(F,\epsilon;\xi,\eta,\phi)=\delta(\xi-\xi')\delta(\eta-\eta')\ .$$

The separation parameter $\beta_n(m,F,\epsilon)$ is determined by requiring u_{1m} to converge (after n nodes) at $\xi\rightarrow\infty$ where the potential rises steadily. The potential falls instead at $\eta\rightarrow\infty$ where u_{2m} oscillates after tunneling through a barrier if ϵ falls in the range of bound-state levels.[7]

Replacement of the bare nucleus of H by a "frozen" ionic core with spherical symmetry—such as occurs in alkali atoms—preserves the invariance of ϵ and m in the set (1) but couples wave functions with different values of n. The n quantum number serves here as the channel index in a scattering process, as the orbital l does in other phenomena. Exchanges of energy and/or angular momentum with the core would be treated by enlarging the set of channels, but we forego this extension for simplicity.

The scattering effect of the ionic core upon the electron states (1) stems from a potential V, the excess of the electron's interaction with the core (including exchange) over its interaction $-e^2/r$ with a bare H^+ ion. Eigenfunctions Ψ_{nm} for the complete potential $-e^2/r+V+eFz$ are constructed by adding to each ψ_{nm} a superposition of the set (1) extending over all channels and energies, but over a single m,

$$\Psi_{nm}(F,\epsilon;\xi,\eta,\phi)=\psi_{nm}(F,\epsilon;\xi,\eta,\phi)+\sum_{n'}\int_{-\infty}^{\infty}d\epsilon'\,\psi_{n'm}(F,\epsilon';\xi,\eta,\phi)\frac{\mathcal{P}}{\epsilon-\epsilon'}\,N^{*}_{n'\epsilon'}\langle n'\epsilon'|K_m^{(so)}(\epsilon)|n\epsilon\rangle N_{n\epsilon}\ . \tag{2}$$

Here $\mathcal{P}$ indicates principal part integration at $\epsilon'\sim\epsilon$, and the coefficients of the superposition are matrix elements of a reaction operator K,[8] from which $N^{*}_{n'\epsilon'}$ and $N_{n\epsilon}$ have been factored out. The ansatz (2) reduces the Schrödinger equation for Ψ_{nm} to an equation for K which we need not solve here. The label "*so*" means that $K^{(so)}$ operates on the eigenfunctions $u_{1m}u_{2m}$ of the outer field[8] normalized independently of ϵ at $(\xi,\eta)\to 0$. This specification makes $K^{(so)}$ "smooth and analytic"[9] in its dependence on ϵ as well as *independent of the Stark field F*, which is negligible wherever V is nonzero. The coefficients $N_{n\epsilon}$ depend instead on F; they are given explicitly in Ref. 6.

The integration over ϵ' in Eq. (2) may seem laborious but is in fact trivial just at $\eta\to\infty$ where (2) serves to determine the channel mixing and the normalization of Ψ_{nm}. Note that the second term of (2) may be viewed as resulting from the application to ψ_{nm} firstly of the operator $K^{(so)}$ and then of the standing-wave Green's function for motion in the Coulomb-Stark (CS) field[8]

$$G^{(\mathrm{CS})}(\vec{r},\vec{r}\,')=\sum_{n'm}\int_{-\infty}^{\infty}d\epsilon'\,\psi_{n'm}(F,\epsilon';\xi,\eta,\phi)\frac{\mathcal{P}}{\epsilon-\epsilon'}\,\psi_{n'm}(F,\epsilon';\xi',\eta',\phi')\ . \tag{3}$$

At $\eta\to\infty$, ψ_{nm} oscillates so rapidly, as a function of ϵ', that its contributions to $G^{(\mathrm{CS})}$ cancel except at $\epsilon'\sim\epsilon$, where they yield[8]

$$G^{(\mathrm{CS})}(\vec{r},\vec{r}\,')=\pi\sum_{n'm}\chi_{n'm}(F,\epsilon;\xi,\eta,\phi)\psi_{n'm}(F,\epsilon;\xi',\eta',\phi'),\quad \eta>\eta'\ . \tag{4}$$

Here χ_{nm} is identified as that solution of the equation for ψ_{nm} which oscillates at $\eta\to\infty$ with the same amplitude as ψ_{nm} but with a 90° phase lag; this identification suffices to define χ_{nm} at all η, but (4) remains qualified by $\eta>\eta'$. Substitution of (3) and (4) reduces Eq. (2) to

$$\Psi_{nm}(F,\epsilon;\xi,\eta,\phi)=\psi_{nm}(F,\epsilon;\xi,\eta,\phi)+\pi\sum_{n'}\chi_{n'm}(F,\epsilon;\xi,\eta,\phi)N^{*}_{n'\epsilon}\langle n'\epsilon|K_m^{(so)}(\epsilon)|n\epsilon\rangle N_{n\epsilon},\qquad (\xi,\eta)>O(1\ \text{a.u.})\ . \tag{5}$$

This reformulation relieves us of any need to consider matrix elements of $K^{(so)}$ off diagonal in (ϵ',ϵ). The diagonal elements are treated next. Note how the integration over ϵ' has served here to isolate relevant aspects of Ψ_{nm} at $\eta\to\infty$, while aspects relevant at $(\xi,\eta)=O(1)$ are considered below; the behavior of Ψ_{nm} at intermediate ranges of (ξ,η) is *not* relevant to us.

Invariance of the ionic core under rotations about its nucleus implies that V and $K^{(so)}$ are diagonal in the orbital quantum number l. Indeed, the Schrödinger equation with the potential $-e^2/r+V$ has solutions analogous to (2) but separable in polar coordinates,

$$F_l^0(\epsilon,r)\,Y_{lm}(\theta,\phi)=\left[f_l^0(\epsilon,r)+\int_{-\infty}^{\infty}d\epsilon'\,f_l^0(\epsilon',r)N^{*}_{l\epsilon'}\frac{\mathcal{P}}{\epsilon-\epsilon'}\,N_{l\epsilon'}\langle l\epsilon'|K^{(so)}(\epsilon)|l\epsilon\rangle\right]Y_{lm}(\theta,\phi)\ . \tag{6}$$

Here $f_l^0(\epsilon,r)$ is a hydrogen radial function normalized to r^l at $r\to 0$ and renormalized to unit energy (at $\epsilon\lesseqgtr 0$) by the separate factor $N_{l\epsilon}$.[9] (The index 0 means "normalized at $r\to 0$," as in Ref. 9.) Reference to the Coulomb (C) Green's function

$$\begin{aligned}G^{(\mathrm{C})}(\vec{r},\vec{r}\,')&=\sum_{lm}Y_{lm}(\theta,\phi)\int_{-\infty}^{\infty}d\epsilon'\,f_l^0(\epsilon',r)N_{l\epsilon'}\frac{\mathcal{P}}{\epsilon-\epsilon'}N^{*}_{l\epsilon'}f_l^0(\epsilon',r')\,Y_{lm}(\theta',\phi')\\&=\pi\sum_{lm}Y_{lm}(\theta,\phi)\bar{g}_l(\epsilon,r)|N_{\epsilon l}|^2 f_l^0(\epsilon,r')\,Y_{lm}(\theta',\phi'),\quad r>r'\ ,\end{aligned} \tag{7}$$

where $\bar{g}_l(\epsilon,r)$ (Ref. 9) lags 90° behind $f_l^0(\epsilon,r)$ at $r\to\infty$, yields the analog of Eq. (5)

$$F_l^0(\epsilon,r)=f_l^0(\epsilon,r)+\pi\bar{g}_l(\epsilon,r)|N_{l\epsilon}|^2\langle l\epsilon|K^{(so)}(\epsilon)|l\epsilon\rangle\ . \tag{8}$$

The reaction matrix element can thus be expressed as

$$\langle l\epsilon|K^{(so)}|l\epsilon\rangle = -\pi^{-1}\tan\delta_l^{(s)}(\epsilon)\,|N_{l\epsilon}|^{-2} \ , \qquad (9)$$

in terms of the phase shift $\delta_l^{(s)}$ of $F_l^0(\epsilon,r)$ with respect to $f_l^0(\epsilon,r)$. This phase shift can be obtained from the zero-field spectrum of bound-state levels of the atom, by quantum-defect analysis,[3,9] or it can be calculated *ab initio* for the ϵ of interest. Note that $\delta_l^{(s)} \neq 0$ for $l \leq 3$ only, as higher partial waves do not penetrate atomic cores.

We come now to our main task of transforming the matrix (9) to the frame of parabolic coordinates. The transformation can be introduced through the expansion of the parabolic ψ_{nm} into spherical harmonics with r-dependent coefficients,

$$\psi_{nm}(F,\epsilon;\xi,\eta,\phi) = N_{n\epsilon}\sum_l b_{nl}(F,\epsilon,m;r)\,Y_{lm}(\theta,\phi) \ . \qquad (10)$$

Since $\psi_{nm}/N_{n\epsilon}$ and $f_l^0 Y_{lm}$ obey equations that differ negligibly at $r \leq O(1\text{ a.u.})$, where $|eFz| \ll |-e^2/r|$, and have analogous normalization, the coefficients b_{nl} must be proportional to $f^0(r)$ at small r and do not depend on F explicitly. However, b_{nl} does depend on F implicitly through the separation parameter β_n of Eq. (1) which results from the quantization at $\xi \to \infty$. It is the restriction to $r \leq O(1)$ which makes the transformation (10) "local." Recalling that $u_{1m}u_{2m} \to (\xi\eta)^{m/2} = r^m \sin^m\theta$ as $(\xi,\eta \to 0)$ while $f_l^0(\epsilon,r) \to r^l$ as $r \to 0$, we write

$$b_{nl}(F,\epsilon,m;r) = a_{lm}(\beta_n,\nu)\,r^l[1+O(r)] \ . \qquad (11)$$

On the right-hand side, ϵ has been replaced by $\nu = (-\epsilon/13.6\text{ eV})^{-1/2}$ and n by β_n of Eq. (1). According to (10) and (11), the coefficients a_{lm} are obtained by projecting the confluent hypergeometric factors of ψ_{nm}, with $F=0$, onto the associated Legendre polynomials $P_l^m(\cos\theta)$,

$$a_{lm}(\beta_n,\nu) = r^{-l}\int_{-1}^{1} d(\cos\theta)\,\sin^{2m}\theta\,P_l^m(\cos\theta) \times F\left[-\beta_n\nu + \tfrac{1}{2}(m+1), m+1, \frac{r(1+\cos\theta)}{\nu}\right] F\left[(\beta_n - 1)\nu + \tfrac{1}{2}(m+1), m+1, \frac{r(1-\cos\theta)}{\nu}\right] \ . \qquad (12)$$

This integral over powers of $\cos\theta$ reduces manifestly to a hypergeometric polynominal.

Specifically, Eq. (12) is known to reduce to a Wigner coefficient,[10]

$$a_{lm}(\beta_n,\nu) = (-1)^l\langle lm|jm_1,jm_2\rangle\left[2\frac{n!\,\Gamma(\nu-n-m)\,\Gamma(\nu+l+1)}{(n+m)!\,\Gamma(\nu-n)\,\Gamma(\nu-l)}\right]^{1/2}\frac{2^l m!^2}{(2l+1)!\,\nu^{l-m}} \ ,$$
$$j = \tfrac{1}{2}(\nu-1), \quad m_1 = (\tfrac{1}{2}-\beta_n)\nu + \tfrac{1}{2}m, \quad m_2 = (\beta_n - \tfrac{1}{2})\nu + \tfrac{1}{2}m \ . \qquad (13)$$

The origin of this result is that the transformations among H wave functions with equal energy are generated by the orbital momentum $\vec{L}$ together with the Lenz vector $\vec{A}$. Each of the combined operators $\frac{1}{2}(\vec{L} \pm \vec{A})$ acts on the wave functions as a spin of magnitude $j = \frac{1}{2}(\nu-1)$, and these two spins add up to l as indicated by (13).[10] The *analyticity of* (12) shows that irrational values of the effective spin j, which become complex for $\epsilon > 0$, are no obstacle to this limited extension of angular momentum algebra. The influence of the Stark field F on the coefficients a_{nl} is implied by the parameters β_n which are themselves determined by the wave-function convergence at $\xi \to \infty$. The reaction matrix elements in Eq. (2) are thus given by (9), (11), and (13) in the form

$$\langle n'\epsilon|K_m^{(so)}(\epsilon)|n\epsilon\rangle = -\pi^{-1}\sum_l a_{lm}^*(\beta_{n'},\nu)\,\tan\delta_l^{(s)}(\epsilon)\,|N_{l\epsilon}|^{-2}a_{lm}(\beta_n,\nu) \ . \qquad (14)$$

In this key result the sum extends only over the few terms with $\delta_l^{(s)} \neq 0$, thus making it unnecessary to consider higher terms of the expansion (10). It is this circumstance that justifies setting $F \to 0$ in the calculation of the transformation coefficients a_{lm} though not in the value of β_n.

Finally, the Stark effect of the photoabsorption spectrum is to be calculated by evaluating the transition dipole moment D_{nm} from the atomic ground state to the various states Ψ_{nm}. These states overlap with the ground state only at $(\xi,\eta) \leq O(1\text{ a.u.})$, where the first term of Eq. (2), ψ_{nm}, is expanded into radial functions $f_l^0(\epsilon,r)$ by (10) and (11). The second term of Ψ_{nm} depends on $\vec{r}$ through the function $G^{(CS)}(\vec{r},\vec{r}\,')$, Eq. (4), which *coincides locally* with $G^{(C)}(\vec{r},\vec{r}\,')$, Eq. (7), because $G^{(CS)}$ and $G^{(C)}$ obey the same inhomogeneous equation at $r \leq O(1)$. Accordingly, the entire Eq. (2) is expanded in terms of (6),

$$\Psi_{nm}(F,\epsilon;\xi,\eta,\phi) \underset{r \leq O(1)}{\longrightarrow} \sum_l F_l^0(\epsilon,r)\,Y_{lm}(\theta,\phi) \times a_{lm}(\beta_n,\nu)\,N_{n\epsilon} \ . \qquad (15)$$

This expansion enables us to expand the desired dipoles D_{nm} in terms of the corresponding zero-field dipoles d^0_{lm} for transition to the eigenstates (6) of $\vec{1}^2$. In the alkali-type atoms considered here, with spherical ionic cores, the only transition allowed in photoabsorption leads to p states; hence only the $l=1$ term of (15) contributes to the spectrum. Thus we have

$$\begin{aligned} D_{nm}(\epsilon) &= \int d\vec{r}\, \Psi^*_{nm} r_m R(r) \\ &= N^*_{n\epsilon} a^*_{1m}(\beta_n, \nu) \\ &\quad \times \int_0^\infty dr\, F^{0*}_1(\epsilon; r) r R(r) \sqrt{1/3} \\ &= N^*_{n\epsilon} a^*_{1m}(\beta_n, \nu) d^0_1(\epsilon) \ , \end{aligned} \tag{16}$$

where r_m equals z for $m=0$ and $\sqrt{1/2}(x+iy)$ for $m=1$, and $R(r)$ is the wave function of the s ground state. The dipole $d^0_1(\epsilon)$ can be obtained from the intensities of zero-field spectral lines, much as the $\delta^{(s)}_l(\epsilon)$ are obtained from the levels, or it can be calculated *ab initio.*

Equation (16) merely distributes the zero-field dipole amplitude d^0_1 linearly among the parabolic channels to yield the D_{nm}. The effect of scattering on the Stark spectrum emerges when the Ψ_{nm} are orthonormalized. In the spherical frame, Eqs. (8) and (9) show F^0_l to be normalized by the coefficient $\cos\delta^{(s)}_l = (1 + tg^2\delta^{(s)}_l)^{-1/2}$. In the parabolic frame the matrix element $\pi N^*_{n'\epsilon} \langle n'\epsilon | K^{(so)}_m(\epsilon) | n\epsilon \rangle N_{n\epsilon}$ plays the same role as

$$\pi |N_{l\epsilon}|^2 \langle l\epsilon | K^{(so)}(\epsilon) | l\epsilon \rangle = -\tan\delta^{(s)}_l(\epsilon)$$

does in Eq. (8). Accordingly, the set Ψ_{nm} is orthonormalized by the matrix $[1 + (\pi N^*_\epsilon K^{(so)}_m N_\epsilon)^2]^{-1/2}$, and the photoabsorption spectrum is proportional to

$$\sum_{n'n} D^*_{n'm}(\epsilon) \{1 + [\pi N^*_\epsilon K^{(so)}_m(\epsilon) N_\epsilon]^2\}^{-1}_{n'n} D_{nm}(\epsilon) \ , \tag{17}$$

with $m=0$ or 1 depending on the incident polarization. [A corrective factor $\mathcal{G}$, which appears in Eqs. (4.15) and (3.17) of Ref. 9 but is very small for Rydberg states, has been ignored here for simplicity but should be considered in more complete treatments.]

Application to the observed Stark spectra of alkali atoms is planned.

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