

Rydberg States of Calcium Fluoride

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We derive the entire singly excited electronic level spectrum of a *dipolar molecule* (CaF) from *atomic properties alone* (the quantum defects of Ca^+). In the approach presented here the motion of the lone electron is treated as a double scattering process involving the closed-shell Ca^{++} and F^- centers with F^- treated as a point charge. The energies of all known electronic states of CaF are well reproduced by the theory. Refinements of the model such as inclusion of the finite volume of F^- or of polarization effects are deferred as are extensions of the model to account for spin-orbit and other fine structure effects.

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Two years ago Murphy *et al.* [1] used optical-optical double resonance fluorescence spectroscopy to study excited states of the calcium fluoride molecule. They uncovered an extended system of previously unknown states, showing that CaF belongs to a novel class of Rydberg molecules (not encompassed by Herzberg's earlier definition [2]). This is one in which the outer electron is bound to a core with total electric charge +1, but where the core itself is subdivided into two distinct entities, a closed-shell calcium ion carrying two positive charges and a closed-shell fluorine atom carrying a single negative charge.

A few years prior to this, Rice, Martin, and Field [3] had already shown that the electronic structure of the lowest states then known of CaF, as well as of several related alkaline earth halides, could be calculated successfully on the simple assumption that these states result from the interaction between a free Ca^+ ion, in various of its lowest states, perturbed and distorted by the field of a negative point charge placed at the position of the fluorine atom. While this "ligand field model" accounts nicely for the lowest states of several alkaline earth halides it cannot be readily extended to the newly observed higher states. This is because with increasing energy the electron cloud of the lone electron on Ca^{++} gradually grows around the F^- ligand until *both* ions are completely surrounded by it, a situation which is not easily handled by the perturbation approach of Ref. [3].

We have here an interesting prototype system. If the F^- indeed acts as a negative point charge it should then be possible to derive the full system of electronic states of CaF from the properties of the Ca^+ ion alone. Specifically, the *three nonzero quantum defects* of Ca^+ , $\mu_s = 0.802$, $\mu_p = 0.432$, $\mu_d = 0.615$, should tell us all that is required to predict the molecular electronic structure of CaF, including the evolution between the limiting situations of an "electron on Ca^{++} " and an "electron on Ca^{++}F^- ." This is therefore a novel application of the concept of "atoms in molecules," and it is one of the simplest ways to turn an atom into a strongly dipolar molecule.

The theoretical development presented below treats the electron core interaction in terms of scattering theory; it is an application of the so-called "generalized quantum defect theory" [4], and it is closely related to the molecular multiple scattering method (MSM) put forward a number of years ago by Dill and Dehmer [5]. We make use of the fact that the Schrödinger equation is *locally separable* in two regions of space (cf. Fig. 1 for reference), namely, outside an appropriately chosen ellipsoid $\xi = \xi_0$ surrounding the two ions (region I), as well as near the surface of the Ca^{++} ion (region III). The main task of the calculation then consists in bridging the gap between those two regions; it is here in the reaction zone II, that the lone electron evolves from an *atomic* into a *molecular* electron or vice versa. We discuss regions I, III, and II in turn.

In region I the lone electron experiences only the electrostatic field $-Z_1/r_1 - Z_2/r_2$, where r_1 and r_2 are the distances from the calcium ($Z_1 = +2$) and the fluorine ($Z_2 = -1$) ions, respectively. The quantum description of its motion is therefore separable in elliptical coordinates $\xi = (r_1 + r_2)/R$ ($1 \leq \xi \leq \infty$) and $\eta = (r_1 - r_2)/R$ ($-1 \leq \eta \leq +1$). Any particular solution ψ_β of the

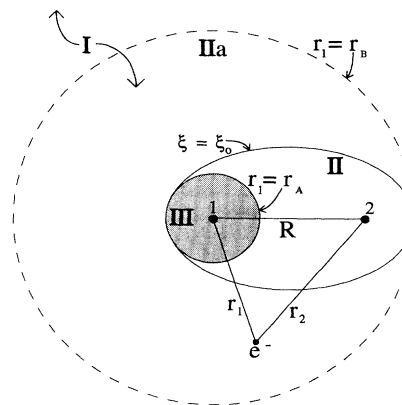


FIG. 1. Various zones relevant to the description of an electron interacting with an atomic core and a point charge.

molecular electronic Schrödinger equation can therefore be written as a superposition of products of elliptical radial channel functions $\tilde{f}_l(\epsilon, \xi)$ and $\tilde{g}_l(\epsilon, \xi)$ (regular and irregular at the origin, respectively) with elliptical angular factors $\tilde{Y}_{\tilde{\lambda}}(\eta, \phi)$,

$$\psi_\beta(\epsilon, \xi, \eta, \phi) = \sum_{\tilde{l}} \tilde{Y}_{\tilde{\lambda}}(\epsilon, \eta, \phi) \frac{1}{(\xi^2 - 1)^{1/2}} \times [\tilde{f}_{\tilde{l}}(\epsilon, \xi) I_{\tilde{l}\beta}(\epsilon) - \tilde{g}_{\tilde{l}}(\epsilon, \xi) J_{\tilde{l}\beta}(\epsilon)]. \quad (1)$$

Here ϵ is the electron energy which may be positive (electronic continuum) or negative (bound state spectrum). λ is the electron orbital angular momentum component with respect to the axis joining atoms 1 and 2. It is a good quantum number as long as the nuclei are kept fixed. The tildes on $\tilde{f}$, $\tilde{g}$, and $\tilde{Y}$ (and on other quantities later in the text) serve to distinguish these functions from their spherical analogs. The differential equations which yield the elliptical functions $\tilde{f}_{\tilde{l}}$, $\tilde{g}_{\tilde{l}}$, and $\tilde{Y}_{\tilde{\lambda}}$ depend on Z_1 , Z_2 , R , and ϵ ; they are well known [6] and will not be repeated here. The calculation of the energy-normalized channel basis functions $\tilde{f}_{\tilde{l}}$ and $\tilde{g}_{\tilde{l}}$ for arbitrary positive ϵ is straightforward and may be performed by any standard numerical propagation scheme. For negative energy it is the main task of generalized quantum defect theory [4,7].

We wish to determine the coefficients $I_{\tilde{l}\beta}$ and $J_{\tilde{l}\beta}$ in Eq. (1) in terms of an adequate set of independent eigensolutions ψ_β . The reactance matrix $K_{\tilde{l}\tilde{l}'}$, or the equivalent quantum defect matrix $\mu_{\tilde{l}\tilde{l}'}$, is then given by

$$K_{\tilde{l}\tilde{l}'}(\epsilon, R) \equiv \tan \pi \tilde{\mu}_{\tilde{l}\tilde{l}'}(\epsilon, R) = \sum_{\beta} J_{\tilde{l}\beta} I_{\tilde{l}'\beta}^{-1}. \quad (2)$$

The matrices **I**, **J**, **K**, and $\tilde{\mu}$ depend on what happens to the lone electron inside the reaction zone II. If both ions were simple point charges, then **J**, and consequently **K** and $\tilde{\mu}$, would be zero. Once the quantum defect matrix $\tilde{\mu}$ is known, the electronic bound state spectrum emerges from the requirement that the wave function vanish for $\xi \rightarrow \infty$. In the framework of generalized quantum defect

theory this leads to the condition that

$$\sum_{\tilde{l}} [\tan \pi \tilde{\mu}_{\tilde{l}\tilde{l}'}(\epsilon, R) + \tan \beta_{\tilde{l}}(\epsilon, R) \delta_{\tilde{l}\tilde{l}'}] Z_{\tilde{l}} = 0 \quad (3)$$

for each elliptical partial wave $\tilde{l}$. The parameter $\beta_{\tilde{l}}$ in Eq. (3) is the so-called accumulated phase at the given energy $\epsilon \leq 0$, which, on division by π , simply gives the number of half oscillations carried out by the regular function $\tilde{f}_{\tilde{l}}(\epsilon, \xi)$ of arbitrary ϵ before it diverges as $\xi \rightarrow \infty$. $\beta_{\tilde{l}}/\pi$ is just the generalization of the familiar effective principal quantum number for a Coulomb field, $\beta_l^{(\text{Coul})}/\pi = \nu^{\text{Coul}} - l = Z(-2\epsilon)^{-1/2} - l$, with the difference that in the general case the relationship between the accumulated phase and the energy is no longer given by the Rydberg equation but must be evaluated numerically. The reader who is not familiar with quantum defect theory may easily convince himself that for a single channel Eq. (3) reduces to the condition $\tilde{\mu} + \beta/\pi = n$ (n integer). In other words, the contributions to the total accumulated phase of the bound state radial wave function arising inside ($\pi\tilde{\mu}$) and outside (β) the reaction zone must add up to a multiple of π .

We next consider the wave function near each of the scattering centers Ca^{++} and F^- , respectively, and, in the spirit of the MSM, we consider each center separately. The $e^- - \text{F}^-$ interaction is repulsive and hence the corresponding scattering phase shifts must be small. We actually set them to zero, thus replacing the fluorine ion by a negative point charge as is done in ligand field theory. By contrast, the scattering off the strongly attractive calcium ion depends sensitively on the internal structure of the latter. Near the doubly charged core the potential term $-Z_1/r_1$ dominates so that the electronic Schrödinger equation becomes *locally separable* in terms of the spherical coordinates r_1, θ_1, ϕ centered on the nucleus 1. Therefore we obtain the constraint on each eigensolution ψ_β in region II that it must reduce to a superposition of *spherical atomic* partial waves on the boundary of the atomic region III, $r_1 = r_A$,

$$\psi_l(\epsilon, r_1, \theta_1, \phi) = Y_{\lambda}(\theta_1, \phi) \frac{1}{r_1} [f_l(\epsilon, r_1) \cos \pi \mu_l - g_l(\epsilon, r_1) \sin \pi \mu_l], \quad (4)$$

where the Y_{λ} are now ordinary spherical harmonics and f_l and g_l are energy-normalized regular and irregular Coulomb functions, respectively. Each component $r_1 \psi_l(r_1)$ is characterized by a *constant* logarithmic derivative on the ion surface $r_1 = r_A$,

$$b_l(r_1) = - \frac{\partial(r_1 \psi_l)/\partial r_1}{(r_1 \psi_l)} = \frac{f'_l(r_1) \cos \pi \mu_l - g'_l(r_1) \sin \pi \mu_l}{f_l(r_1) \cos \pi \mu_l - g_l(r_1) \sin \pi \mu_l}. \quad (5)$$

The coefficients μ_l in Eqs. (4) and (5) are simply the known atomic quantum defects of the Ca^+ ion. Equation (5) expresses the fact that the knowledge of these quantum defects is tantamount to the knowledge of a corresponding set of radial boundary conditions b_l on a suit-

ably chosen spherical surface near the Ca^{++} nucleus.

We now turn to the problem of constructing a set of eigensolutions ψ_β valid throughout the reaction zone II, which have the correct logarithmic derivatives on the III/II boundary as required by Eq. (5) and which may be matched to the asymptotic form Eq. (1) at the II/I boundary. We introduce at this point the auxiliary region IIa which is the region between the two spherical surfaces $r_1 = r_A$ and $r_1 = r_B$ centered on the metal nucleus 1 and enclosing the ellipsoid $\xi = \xi_0$ (see Fig. 1), and the smaller atomic core surface $r_1 = r_A$. The advantage of using region IIa is that it may be spanned by a set of spherical free-particle eigenfunctions defined for positive as well as negative energy that have well defined boundary condi-

tions on the edge of region III. These are

$$\psi_{m\lambda}(r_1, \theta_1, \phi) = Y_{\lambda}(\theta_1, \phi) \frac{1}{r_1} [c_{m\lambda} \sin(k_{m\lambda} r_1) + d_{m\lambda} \cos(k_{m\lambda} r_1)] \quad (\epsilon_{m\lambda} = \frac{1}{2} k_{m\lambda}^2 \geq 0), \quad (6a)$$

$$\psi_{m\lambda}(r_1, \theta_1, \phi) = Y_{\lambda}(\theta_1, \phi) \frac{1}{r_1} [c_{m\lambda} e^{\kappa_{m\lambda} r_1} + d_{m\lambda} e^{-\kappa_{m\lambda} r_1}] \quad (\epsilon_{m\lambda} = -\frac{1}{2} \kappa_{m\lambda}^2 \leq 0). \quad (6b)$$

The coefficients c and d in Eqs. (6) are determined for each function by the appropriate atomic boundary condition $b_l(r_1=r_A)$ [Eq. (5)] on the one hand, and by an additional condition $b_l(r_1=r_B)$ at the outer boundary of region IIa on the other hand. This second condition is regarded as a free parameter at this stage and is chosen to be the same for all partial components l , $b_l(r_1=r_B) \equiv b(r_B)$. The set of functions $\psi_{m\lambda}(b_B)$ defined by Eq. (6) is *orthonormal* and *discrete* as indicated by the radial quantum number m .

The Hamiltonian in region IIa for $r_A \leq r_1 \leq r_B$, is simply the electrostatic interaction between the lone electron and the two charges Z_1 and Z_2 . The matrix representation of the potential energy for each value of λ is given by the integrals

$$H_{m\lambda, m'\lambda'}^{(\lambda)}(b(r_B)) = \iint \psi_{m\lambda}^*(r_1, \theta_1, \phi) \left[-\frac{Z_1}{r_1} + \frac{l(l+1)}{2r_1^2} - \frac{Z_2}{(r_1^2 - 2r_1 R \cos \theta_1 + R^2)^{1/2}} \right] \psi_{m'\lambda'}(r_1, \theta_1, \phi) r_1^2 \sin \theta_1 dr_1 d\theta_1 d\phi. \quad (7)$$

All matrix elements depend parametrically on the boundary condition $b(r_B)$ and are of course diagonal in the quantum number λ .

Diagonalization of the Hamiltonian matrix Eq. (7) yields a set of eigenenergies $\epsilon_\beta^{(\lambda)}(b(r_B))$ and eigenfunctions $\psi_\beta^{(\lambda)}(b(r_B))$ valid everywhere in region IIa and thus also in the enclosed region II. Since we wish to match the eigenfunctions ψ_β to the asymptotic form of Eq. (1) at a *preselected energy* ϵ , the parameter $b(r_B)$ must be varied until one of the eigenvalues ϵ_β coincides with ϵ . This is the iterative eigenchannel R -matrix procedure of Fano and Lee [8], with the difference that here boundary conditions are imposed on an *inner* as well as on an *outer* boundary. There will be as many distinct eigenvalues $b_\beta(r_B)$ as there are partial waves l in the basis set Eq. (6). Their inverses are just the eigenvalues of the conventional R matrix [9]. Rather than varying $b(r_B)$ explicitly we have used the equivalent noniterative variant [10] of the eigenchannel R -matrix method which yields the eigenvalues b_β directly as the solutions of a generalized eigenvalue problem.

Once the set of eigenfunctions ψ_β spanning region IIa has been evaluated for the desired energy ϵ , the values $\psi_\beta(\xi_0)$ and derivatives $\psi'_\beta(\xi_0)$ with respect to ξ on the surface of the reaction zone II are also known. The matrices **I** and **J** are then calculated through matching by means of Eq. (1) and its derivative. The result is

$$I_{i\beta} = \pi(\tilde{g}'_i u_{i\beta} - \tilde{g}_i u'_{i\beta}), \quad J_{i\beta} = \pi(\tilde{f}'_i u_{i\beta} - \tilde{f}_i u'_{i\beta}), \quad (8a)$$

where primes refer to differentiation with respect to ξ and where we have made use of the fact that the Wronskian $W(\tilde{f}_i, \tilde{g}_i)$ equals $1/\pi$. The coefficients u result from expanding ψ_β on the reaction surface in terms of the orthonormal "surface harmonics" $\tilde{Y}_{\lambda}(\eta)$:

$$u_{i\beta}(\xi) = \int \tilde{Y}_{\lambda}^*(\eta, \phi) [(\xi^2 - 1)^{1/2} \psi_\beta^{(\lambda)}(\xi, \eta, \phi)] d\eta d\phi. \quad (8b)$$

The right-hand side of Eq. (8) is evaluated for $\xi = \xi_0$; the

resulting matrices **I** and **J** are independent of ξ_0 . Use of Eq. (2) then completes the calculation of the elliptical quantum defect matrix $\tilde{\mu}_{\tilde{l}\tilde{m}}$.

In a typical calculation we have taken the values $r_A = 0.8$ a.u., $r_B = 6.5$ a.u., $\xi_0 = 2.7$, and $\epsilon = -0.01$ a.u. corresponding to $v^{(\text{Coul})} \sim 7$. $R = 3.54$ a.u. is the equilibrium internuclear distance of CaF^+ . The Ca^+ quantum defects for $l=0-2$ used are those quoted at the beginning of this Letter. For $l \geq 3$ we set $\mu_l = 0$. We have found that ten radial components m and five angular components l in the basis Eq. (6) yielded converged results. The Rydberg energies $\epsilon_{n\lambda}(R)$ are then calculated from the $\tilde{\mu}$ matrices by means of the generalized Rydberg equation (3).

The results are conveniently displayed with reference to the effective principal quantum number

$$v_{n\lambda}^{(\text{Coul})} = \frac{Z_1 + Z_2}{(-2\epsilon_{n\lambda})^{1/2}}, \quad n = 1, 2, \dots, \quad (9)$$

referring to the Coulomb system with total charge $Z_1 + Z_2 = +1$. The effective quantum numbers thus evaluated combine contributions due to the core dipole field and higher multipole components as well as penetration into the Ca^{++} core. Figures 2(a) and 2(b) are plots of $v_{n\lambda}^{(\text{Coul})}(\text{modulo } 1)$ vs $v_{n\lambda}^{(\text{Coul})}$ and compare the experimental values from various sources [1,11,12] (dots) with the theoretical results (lines). It can be seen that the agreement is satisfying. An important point to note is that the theory predicts correctly the lowest state of each of the six known Rydberg series; the successful calculation of the ground state at $v^{(\text{Coul})} = 1.541$ (observed 1.528) is particularly gratifying and shows that even the ground state of CaF can be viewed as a Rydberg state in the generalized sense employed here. In terms of energy, the lowest states are reproduced to within 0.1–0.2 eV, with a smaller mean error than in all previous calculations [3,13,14]. The agreement is about 10 times better for the higher states.

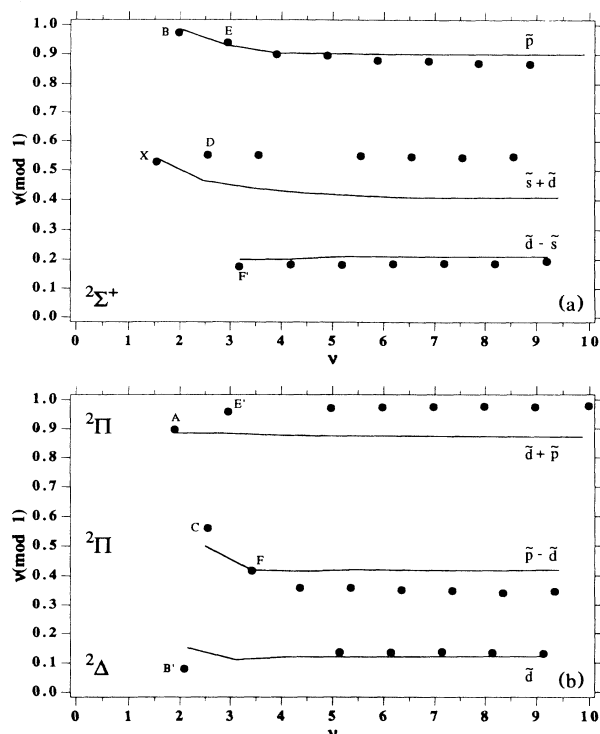


FIG. 2. Effective principal quantum numbers (modulo 1) of CaF plotted vs their absolute values. (a) $2\Sigma^+$ states; (b) 2Π and 2Δ states. Dots, observed values; lines, calculated values. All presently known electronic states of CaF are included. The labels at the right indicate for each Rydberg series the dominant elliptical angular momentum components $\bar{l}$ including their phases.

The theoretical method presented here opens up a range of avenues to be pursued in the future. First of all, it should be possible to predict several finer features of the CaF states such as the spin-orbital coupling, which is a probe of the wave function near the Ca nucleus [15]. The evolution of the effective principal quantum numbers $v_{nl}^{(\text{Coul})}$ as functions of the internuclear distance R may be calculated, giving in effect the electronic potential energy curves which are the goal of standard quantum-chemical calculations. In addition the R dependence of the quantum defect matrix elements $\bar{\mu}\bar{\nu}$ will allow the coupling between vibrational and electronic degrees of freedom to be calculated, i.e., the breakdown of the Born-Oppenheimer separation. Experimental information on all of these effects exists already [16].

Second, the method outlined here should allow us to deal with dipolar systems in general. Obvious candidates are the alkaline earth halides other than CaF, such as BaF for which s, p, d as well as f states are core penetrating and the corresponding more extended system of states ($\bar{l}=0-3$) has indeed been found [17]. The rare gas hydrides constitute another class of dipolar systems which have recently been studied [18] extensively, and where a comprehensive interpretation of the electronic structure is

still lacking.

Finally, the present work should lead to a considerable extension of the multiple scattering method for calculating e^- -molecule scattering processes [5]. This will involve representing the second center (here F^-) by an atomic core region with associated quantum defects as has been done here for center I. Our diagonalization procedure then removes a major drawback of the MSM, namely, the need to have a constant potential between the centers. Charged constituent atoms can thus be treated as well as neutral ones, and polarization terms are incorporated readily.

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- [1] J. E. Murphy, J. M. Berg, A. J. Merer, Nicole A. Harris, and R. W. Field, Phys. Rev. Lett. **65**, 1861 (1990).
- [2] G. Herzberg, Annu. Rev. Phys. Chem. **38**, 27 (1987).
- [3] S. Rice, H. Martin, and R. W. Field, J. Chem. Phys. **82**, 5023 (1985).
- [4] C. H. Greene, A. R. P. Rau, and U. Fano, Phys. Rev. A **26**, 2441 (1982); F. Mies, J. Chem. Phys. **80**, 2514 (1984).
- [5] D. Dill and J. L. Dehmer, J. Chem. Phys. **61**, 692 (1974).
- [6] See, e.g., R. A. Buckingham, in *Quantum Theory I. Elements*, edited by D. R. Bates (Academic, New York, 1961), pp. 121-132.
- [7] B. Yoo and C. H. Greene, Phys. Rev. A **34**, 1635 (1986); Ch. Jungen (to be published).
- [8] U. Fano and C. M. Lee, Phys. Rev. Lett. **31**, 1573 (1973).
- [9] U. Fano and A. R. P. Rau, *Atomic Collisions and Spectra* (Academic, New York, 1986).
- [10] H. Le Rouzo and G. Raseev, Phys. Rev. A **29**, 1214 (1984); Chris H. Greene, Phys. Rev. A **28**, 2209 (1983).
- [11] J. D'Incan, C. Effantin, A. Bernard, J. Vergès, and R. F. Barrow, J. Phys. B **24**, L71 (1991).
- [12] N. A. Harris and R. W. Field, J. Chem. Phys. (to be published).
- [13] T. Törring, W. E. Ernst, and J. Kändler, J. Chem. Phys. **90**, 4927 (1989).
- [14] P. Bündgen, B. Engels, and S. D. Peyerimhoff, Chem. Phys. Lett. **176**, 407 (1991).
- [15] J. M. Berg, J. E. Murphy, N. A. Harris, and R. W. Field (to be published).
- [16] J. E. Murphy, Ph.D. thesis, Massachusetts Institute of Technology, 1992.
- [17] Z. Jakubek (private communication).
- [18] I. Dabrowski, G. Herzberg, B. P. Hurley, R. H. Lipson, M. Vervloet, and D.-C. Wang, Mol. Phys. **63**, 289 (1988).