

Adventures of a Rydberg electron in an anisotropic world

William Clark and Chris H. Greene

Department of Physics and JILA, University of Colorado, Boulder, Colorado 80309-0440

The study of subtle interactions in atomic and molecular systems has stirred scientific curiosity since the dawn of quantum mechanics. Even today, research into perturbative long-range interactions continues to push into new territory, driven largely by the experimental capabilities of Rydberg state spectroscopy to detect effects of extremely weak interactions. While static long-range multipole interactions have been studied for years, the presence of dynamic terms that involve both position and momentum operators has been demonstrated only surprisingly recently. In this paper we document the existence of an effective vector interaction term in the long-range potential experienced by a moving charged particle in the presence of an anisotropic ionic core. In contrast to ordinary static quadrupole or dipole interaction terms, the existence of this vector interaction hinges on the motion of the distant charge as it roams beyond the confines of the core. [S0034-6861(99)00703-5]

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I. INTRODUCTION

The astonishing precision of high resolution Rydberg state spectroscopy provides a revealing probe of small and large perturbations. The field has progressed tremendously during the half century since the crucial measurement of the Lamb shift (Lamb and Retherford, 1947; Lamb and Retherford, 1950). It is now possible to measure some of the smallest forces in nature through their tiny influences on atomic and molecular energy levels. The measurement of the electroweak interaction and of nuclear anapole moments in table-top atomic physics experiments (Wood *et al.*, 1997) has had important implications in nuclear and high energy physics. Other groups (Sturuss *et al.*, 1988; Arcuni *et al.*, 1990; Sturuss *et al.*, 1991; Ward *et al.*, 1996; Jacobson *et al.*, 1997) have attempted in recent years to make an experimental measurement of the “Casimir force” predicted

to affect the spectra of Rydberg levels (Spruch, 1986). While the existence of such a force is a clearcut implication of atomic theory, it has not yet been conclusively observed in a Rydberg atom or molecule.

Much of the physics community’s interest in this subject stems from the ability of Rydberg spectroscopists to probe small and subtle interactions. In order to understand such tiny interactions, however, it is crucial to first understand quantitatively the energy level shifts and perturbations associated with the quantum mechanics of a Rydberg electron that experiences “simple electrostatic interactions.” These contributions are often subtracted from the measured Rydberg energy level in order to expose the energy shift or splitting that is of interest in any particular experiment.

The present Colloquium article chronicles a surprising development this decade that has resulted in the discovery of “new physics” in the ostensibly simple motion of a Rydberg electron (or other charged particle) moving in the field of an anisotropic ionic core. To set the stage for this discovery, consider first the better-understood problem of an electron that roams beyond an isotropic, closed-shell ionic core. In addition to the net Coulomb attraction towards the ion, the electron also polarizes the ion, inducing an electric dipole moment whose magnitude decreases in proportion to the inverse squared distance r between the electron and ion. The coefficient of proportionality is the polarizability α of the ionic state. Several studies (Dalgarno *et al.*, 1968; Seaton and Steenman-Clark, 1977; Drachman, 1982) have treated this system and shown that an adiabatic treatment of the electron radial coordinate leads to an effective potential energy $V_{\text{pol}}(r) = -(\alpha/2r^4)$ at large values of r . (Except where stated otherwise, we adopt atomic units, in which $e = \hbar = m_e = 1$.)

Comparatively few theoretical formulations have developed a description of a charged particle that interacts with an anisotropic core possessing nonzero angular momentum. In atomic physics, some examples include Dalgarno *et al.* (1968), Seaton and Steenman-Clark (1977),

Drachman (1982), while in molecular physics, a perturbative scheme has been developed to interpret a class of experiments (Eyler and Pipkin, 1983; Sturuss *et al.*, 1988; Sturuss *et al.*, 1991). Also, Herzberg and Jungen (1982), Jungen *et al.* (1989), and Jungen *et al.* (1990) have formulated and applied a more general nonperturbative scheme to describe molecular Rydberg states. An anisotropic core opens up some new types of interactions that are absent for an isotropic core. The first is an interaction potential $(Q/r^3)P_2(\cos\theta)$ between the distant electron and the electric quadrupole moment (Q) of the core, which can be nonzero if the core angular momentum J is greater than or equal to 1. The core anisotropy causes a second modification as well: now the $1/r^4$ polarizability interaction contains both a *scalar* contribution $-(\alpha^{(s)}/2r^4)$ and a *tensor* contribution. The latter is sometimes written as $-(\alpha^{(t)}/2r^4)P_2(\cos\theta)$. Note that θ is the angle between a symmetry axis in the ionic core and the unit position vector \hat{r} of the Rydberg electron.

The theory of Rydberg systems has traditionally been divided among perturbative approaches that form the basis for polarization models, and multichannel formulations like R-matrix and multichannel quantum defect theory (MQDT) (Aymer *et al.*, 1996). When the Rydberg electron has a large orbital angular momentum ℓ , the centrifugal repulsion keeps the electron beyond its inner turning point ($r_t \approx \frac{1}{2}\ell(\ell+1)$) most of the time, which eliminates most short-range interactions such as exchange and partial screening of the nuclear charge. Exploited particularly as sensitive probes of long-range interactions, the perturbative approaches have been useful tools for both theory and experiment. Of course perturbative approaches are limited to systems for which the coupling among Rydberg states is weak or negligible. The more rigorous basis set expansions of nonperturbative multichannel formulations, on the other hand, can describe this complicated physics, but remain limited in the physical insight and interpretation that they yield readily.

The recent prediction, measurement, and confirmation of a vector interaction (Zygelman, 1990; Clark *et al.*, 1996; Ward *et al.*, 1996; Clark and Greene, 1997), in Rydberg systems with nonspherical ionic cores, highlights the need to better understand the nature of nonrelativistic long-range interactions. The vector interaction is a term in the effective long-range potential energy which has the structure

$$\beta_v \frac{\vec{L}_c \cdot \vec{\ell}}{r^6}. \quad (1)$$

Here \vec{L}_c and $\vec{\ell}$ denote the orbital momenta of the ionic core and the Rydberg electron, respectively, and r is the distance between the Rydberg electron and the core. While we use the term “vector interaction” to describe the $\vec{L}_c \cdot \vec{\ell}$ structure in Eq. (1), it is of course an overall scalar, whereby it remains consistent with the required conservation of total angular momentum of the core-ion system. It is the *only* nonzero term in the effective long-range potential with radial exponent $n \leq 6$ that has an

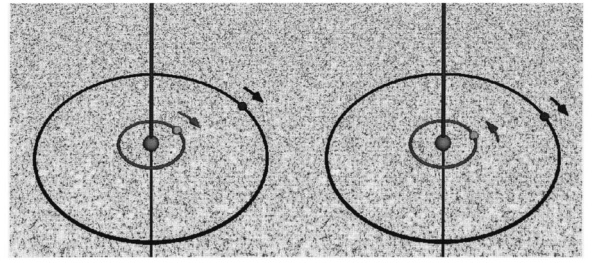


FIG. 1. Classical orbits of a Rydberg electron around a core consisting of an electron with angular momentum circling about a nucleus. The interaction energy associated with the vector interaction term in Eq. (1) has opposite sign depending on whether the angular momenta are parallel (left) or antiparallel (right).

odd tensorial rank for the ionic degrees of freedom. (Other odd-rank terms such as the dipole or octopole terms of the electrostatic interaction fail to survive in first-order, for the typical situation in which the ionic states possess definite parity.) Strictly speaking, the operators \vec{L}_c and $\vec{\ell}$ in Eq. (1) are even parity *pseudovectors* rather than odd-parity vectors, with respect to separate transformations of the ionic or Rydberg electron degrees of freedom. But for brevity we refer to their scalar product throughout this paper as a “vector interaction.”

Traditionally, long-range interaction potentials have taken the form of purely coordinate-dependent potential energy functions. Equation (1) departs from this tradition through its inclusion of angular momentum operators in the long-range potential. The physical implications of this angular momentum dependence are dramatized in Fig. 1, which shows two similar pairs of coplanar classical orbits for a two-electron atom. In a strictly adiabatic treatment of the outer Rydberg electron motion, the interaction energy would be the same for these two orbit configurations. Owing to the presence of interactions like Eq. (1), however, the interaction energies contain a term that has opposite sign for antiparallel and parallel orbits. We return in Sec. IV to this example, and analyze this simple coplanar configuration from both a classical and a quantum mechanical perspective. Both analyses predict that the left-hand state, with parallel angular momenta, has lower energy than the right-hand state with antiparallel angular momenta.

Figure 2 demonstrates that there are simple, experimentally measurable consequences caused in the pattern of Rydberg state energy level splittings by the vector interaction. Shown are the splittings one expects for the energy eigenstates $E_L(L_c, \ell)$ associated with different eigenvalues $L(L+1)$ of the total squared angular momentum $\vec{L} = \vec{L}_c + \vec{\ell}$. The level splittings are for a system for which we can ignore the spin of the Rydberg electron and consider only its orbital angular momentum $\ell = 6$ and that of the core ($L_c = 2$ for this example). If there were only isotropic (scalar) terms in the long-range electron-core interaction potential, all of the lev-

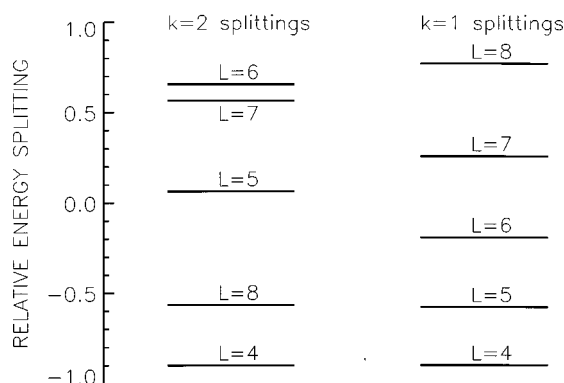


FIG. 2. Pattern of relative energy level splittings caused by the conventional anisotropic tensor ($k=2$) terms and by the vector ($k=1$) interaction term of Eq. (1). The splittings shown are for a quantum mechanical Rydberg atom of total angular momentum L , where the ionic core has angular momentum $L_c=2$ and the Rydberg electron has orbital angular momentum $\ell=6$. The spin of the Rydberg electron has been neglected in this illustration.

els in Fig. 2 would be degenerate. The presence of core anisotropy is well known to produce terms of tensorial rank $k=2$, however, in the form of a quadrupole moment and a tensor polarizability interaction as discussed above. These anisotropic interactions cause a splitting among the different energy levels $E_L(L_c, \ell)$ as is depicted in the left-hand portion of Fig. 2. The L dependence of the splittings is controlled by a Wigner $6J$ -coefficient:

$$(-1)^L \begin{Bmatrix} L_c & \ell & L \\ \ell & L_c & k \end{Bmatrix}.$$

Notice in particular how the highest ($L=8$) and lowest ($L=4$) energy levels deviate in the same direction from the center of the distribution for the “ordinary” $k=2$ tensorial interactions, while in contrast, the $k=1$ vector interaction of Eq. (1) results in energy shifts of opposite sign for the extremes in total angular momentum. This is expected since the recoupling coefficient in the large L limit has an L dependence governed by $\approx P_k(\hat{L}_c \cdot \hat{\ell})$, with the odd- k Legendre polynomials odd in parity. This qualitative difference between splitting patterns induced by odd k and even k terms in the interaction potential can be measured in the laboratory.

The vector interaction is an example of a dynamic angular interaction that physically reflects the inability of the ionic core to instantaneously adjust to the angular motion of the Rydberg electron. Here is the classical picture of this effect: as the Rydberg electron “orbits” the core, the core tries to repolarize in the direction of the Rydberg electron, but fails to do so fast enough and its dipole moment lags behind. This nonadiabatic behavior qualitatively resembles retardation, but it originates in the nonrelativistic dynamics of the Rydberg electron rather than in the finite speed c at which interactions propagate through space (Spruch, 1986; Babb and Spruch, 1994).

In this article we sketch the development of a systematic adiabatic treatment of Rydberg systems that includes these nonadiabatic effects explicitly. We stress the qualitatively new insights that have emerged from this line of research in the present decade. Experimental observations of Ne Rydberg states (Ward *et al.*, 1996) have recently confirmed the existence of the vector interaction and its importance in Rydberg state spectroscopy.

II. ADIABATIC THEORY

A. Adiabatic representation

The concept of adiabaticity has been used extensively in atomic and molecular physics. The earliest application was the extremely useful Born-Oppenheimer approximation, which provides the entire framework used today to understand the low vibrational states of diatomic molecules. The approximation starts from the slowness of the nuclear motion compared with the molecular electrons; in consequence, the electronic properties of the system acquire a relatively weak parametric dependence on the internuclear separation. In other words, the slow nuclear motion leads to an approximate separation of the nuclear and electronic degrees of freedom.

This approach can be extended to many other problems in physics. The validity is immediately clear if the adiabatic degree of freedom is “slow” compared to all other degrees of freedom in the system. In Rydberg atoms and molecules it is the radial coordinate r of the Rydberg electron that serves as the best adiabatic coordinate.

A Rydberg atom or molecule with high angular momentum is a simple quantum system involving an electron ($\ell \geq 5$) and a relatively isolated ionic core. The slow-moving Rydberg electron can be regarded as a probe of the weak electrostatic properties of the ionic core: properties like the permanent quadrupole and higher multipole moments and the polarizabilities of the relevant ionic states. The large spatial separation between the Rydberg and core electrons causes Rydberg electron spin effects (such as exchange) to be negligible. The absence of exchange between the Rydberg electron and the core leads to the choice of coupling scheme as $(J_c \ell)K$ coupling (Pruvost *et al.*, 1991). In this scheme, the total angular momentum J_c of the fast core electrons is coupled with the orbital momentum ℓ of the slow Rydberg electron to form a resultant K . (The quantum number K then acts as the “total angular momentum” of the atom in most of our derivations below.)

The centrifugal repulsion of the high- ℓ Rydberg electron forces it to roam far beyond the confines of the core. A simple representation of the wave function for such a system uses an r -independent basis set $\{\phi_i(\omega)\}$, where ω denotes all other coordinates of the system (including spin) besides r . The $\{\phi_i(\omega)\}$ are the complete set of ionic energy eigenstates, whose angular momenta are coupled with the orbital functions Y_{lm} of the Rydberg electron. This ansatz for a Schrödinger eigenstate

leads to a set of coupled radial equations that are usually called the “close-coupling equations” (without exchange) in atomic physics. The radial function $M_i(r)$ in this expansion ($\sum_i \phi_i(\omega) M_i(r)$) can be viewed as the wave function for radial motion within the i th ionic channel of the system. A diagonal matrix element $V_{ii}(r)$ of the core-Rydberg potential energy of interaction in this representation, when added to the centrifugal repulsion term and to the ionic energy level E_i in channel i , constitutes an effective “potential curve” that governs the radial motion of the Rydberg electron in that channel. Off-diagonal matrix elements $V_{ji}(r)$ can be viewed as causing transitions of the electron from the i th electron-core channel to the j th channel.

The full effective potential matrix that governs the Rydberg electron radial motion that enters the conventional close-coupling (CC) equations without exchange is

$$V_{ij}^{CC}(r) = \left(\frac{\ell_i(\ell_i+1)}{2r^2} - \frac{1}{r} + E_i \right) \delta_{ij} + V_{ij}(r). \quad (2)$$

Here ℓ_i is the orbital momentum of the Rydberg electron in channel i . Unless stated otherwise, matrix elements involve integrals over all coordinates (ω) (and traces over all spins) in the problem, except for the radial coordinate of the Rydberg electron. (The spin of the Rydberg electron is ignored for the remainder of this article.) Note that we have split off the dominant Coulomb interaction $-(1/r)$, whereby the remaining potential matrix $V_{ij}(r)$ can be written as an asymptotic series in $1/r$, with the leading term being of order r^{-2} as $r \rightarrow \infty$.

B. Adiabatic close-coupling equations

The basis set $\{\phi_i(\omega)\}$ used in the conventional close-coupling equations are independent of the radial coordinate r of the Rydberg electron, which means that the resulting representation does not describe the increasing polarization of the core electrons during close encounters. That physics is incorporated into the standard close coupling equations only through off-diagonal channel coupling, which is difficult to visualize. Accordingly, we introduce a representation that builds the predominant dynamical effects of electron-core interactions into a more useful effective potential energy curve. As in the molecular Born-Oppenheimer approach, these potential curves are obtained by diagonalization of an “adiabatic Hamiltonian” $\hat{H}_{r=\text{const}}$ in which derivative operators with respect to the adiabatic coordinate r have been discarded. The resulting adiabatic eigenstates $\Phi_\mu(r; \omega)$ form (at every value of r), like the $\{\phi_i(\omega)\}$ discussed above, a complete orthonormal set in the coordinates ω . The adiabatic approximation is valid in our present context if the system remains confined within a single adiabatic channel as the Rydberg electron roams slowly beyond the confines of the core. To be explicit, the

adiabatic potentials $U_\mu(r)$ and eigenstates $\Phi_\mu(r; \omega)$ are defined as parametrically r -dependent solutions of the linear eigenvalue problem:

$$\hat{H}_{r=\text{const}} \Phi_\mu(r; \omega) = U_\mu(r) \Phi_\mu(r; \omega). \quad (3)$$

In the representation $\{\phi_i(\omega)\}$, the matrix of the adiabatic Hamiltonian operator $\hat{H}_{r=\text{const}}$ reduces to $V^{CC}(r)$. The adiabatic channel functions are r -dependent superpositions of the ionic core states. They contain information concerning the instantaneous interactions between the Rydberg electron and the core, and provided r varies slowly, concerning the approximately conserved properties of the electron-core system. Expansion of the total wave function for the system in terms of the adiabatic channel functions

$$\Psi(r, \omega) = \frac{1}{r} \sum_\mu F_\mu(r) \Phi_\mu(r; \omega), \quad (4)$$

transforms the Schrödinger equation into a set of coupled radial equations. These can be written in matrix form as

$$\left[-\frac{1}{2} \left(\underline{I} \frac{d}{dr} + \underline{P}(r) \right)^2 + \underline{U}(r) - E \underline{I} \right] \underline{F}(r) = 0, \quad (5)$$

where the derivative coupling matrix is defined by

$$P_{\mu\nu}(r) = \left\langle \Phi_\mu \left| \frac{\partial}{\partial r} \right| \Phi_\nu \right\rangle. \quad (6)$$

In this paper we adopt Greek letters to label the adiabatic channels. At sufficiently large distances $r \rightarrow \infty$, each adiabatic channel converges to one of the ionic channels labeled by Roman letters in the primitive close-coupling representation.

In contrast to the primitive close-coupling representation, in which the coupling among the ionic channels enters through the potential matrix V^{CC} , the coupling of our *adiabatic channels* enters through a derivative matrix $P_{\mu\nu}(r)$ that modifies the radial momentum operator. Thus the P matrix accounts for all nonadiabatic or inelastic effects that arise because the slow Rydberg electron is “not quite slow enough.” For most of the regimes discussed in this review, the off-diagonal derivative couplings are small compared with the diagonal adiabatic potentials. Under these conditions, the motion of the system remains confined within a single adiabatic channel to an excellent approximation. As we discuss below, the analogy between the modified radial momentum operator and the field-theory notion of “minimal coupling” (Zygelman, 1990) permits some of the long-range interactions to be viewed as non-Abelian gauge fields.

C. Adiabatic potentials and postadiabatic corrections

The Born-Oppenheimer approximation, which neglects the channel coupling matrix $P(r)$ altogether, is adequate for many purposes. To achieve higher accuracy or to treat higher energy processes, however, it is important to include some effects of $P(r)$. One natural

approach to this problem seeks an approximate single-channel form for the radial Schrödinger equation, such as

$$\left(-\frac{1}{2} \frac{d^2}{dr^2} + u_\mu(r, E) - E \right) F_\mu(r) = 0, \quad (7)$$

in which we have introduced a new effective potential $u_\mu(r, E)$ that depends on the adiabatic potentials $\{U_\nu(r)\}$, the derivative couplings, and the energy of the system E in some simple algebraic way.

The post-adiabatic theory of Klar and Fano (Klar and Fano, 1976; Klar, 1977), later generalized by Aquilanti (Aquilanti *et al.*, 1994), is such a method that includes perturbative derivative coupling effects through an iterative algebraic procedure. The main idea is to transform the original adiabatic equation (5) into a set of coupled single-channel equations where the new coupling arises from terms proportional to $P(r)$ or $(d/dr)P(r)$. This “postadiabatic procedure” can be iterated, in principle, which will (hopefully) reduce the coupling strength in each successive iteration.

For our purposes we use only the first iteration of the procedure, for which the effective potential is given by

$$u_\mu(r, E) \approx U_\mu(r) - \frac{1}{2} (P^2)_{\mu\mu} + 2(E - U_\mu(r)) \sum_\nu \frac{|P_{\mu\nu}|^2}{U_\mu(r) - U_\nu(r)}. \quad (8)$$

The perturbative condition $P_{\mu\nu}^2(r) \ll |U_\mu(r) - U_\nu(r)|$ should be satisfied at all r relevant in the problem, but this should always be satisfied for sufficiently high ℓ states of Rydberg systems. A first immediate implication of the nonadiabatic corrections is an increase in the potential energy due to the repulsive energy-independent diagonal term $(-P^2)_{\mu\mu}$. Inclusion of this term in molecular problems is often called the “adiabatic approximation” as opposed to the strict Born-Oppenheimer approximation which neglects $P(r)$ completely. This term is usually written as a second-derivative coupling matrix in that context, but it is equivalent to our form as the square of the first-derivative matrix (see Klar and Fano, 1976). A second implication is the presence of an energy-dependent contribution; its sign can vary from state to state, but for the channel of lowest energy, it generally (Klar and Klar, 1978) makes the effective post-adiabatic potential $u_\mu(r, E)$ increasingly attractive as the energy increases above threshold.

The derivative couplings $P_{\mu\nu}(r)$ can be computed, for instance, by using the Hellman-Feynman theorem. The diagonal derivative couplings vanish, that is $P_{\mu\mu}(r) = 0$, since the P matrix is skew symmetric, and the off-diagonal terms are given by

$$P_{\mu\nu}(r) = \frac{\langle \Phi_\mu | \frac{\partial}{\partial r} \hat{H}_{r=\text{const}} | \Phi_\nu \rangle}{U_\nu(r) - U_\mu(r)}. \quad (9)$$

The partial derivative of the adiabatic Hamiltonian is readily evaluated analytically. This form of the deriva-

tive coupling matrix clearly demonstrates the apparently singular behavior when two channels of common symmetry are nearly degenerate ($U_\mu(r) \approx U_\nu(r)$). This is mainly signalling a failure of the adiabatic (and postadiabatic) notion that the dynamics can be boiled down to a single effective channel. At such a near degeneracy the physics must inherently involve both of the strongly coupled, nearly degenerate channels; in other words, an “avoided crossing” of this type can redistribute radial flux among the strongly coupled channels.

D. Perturbative adiabatic diagonalization for nondegenerate channels

In Rydberg atoms and molecules with high orbital angular momentum (e.g., typically $\ell \geq 5$), the dominant electrostatic interaction between the Rydberg electron and the ionic core is the dipole moment which goes as $1/r^2$. Since a typical inner turning radius is $r_t \approx \ell(\ell + 1)/2$ for a Rydberg electron near zero energy, all electrostatic interactions are perturbative compared to the screened-charge term $-1/r$. The small values of the electrostatic matrix elements $V_{ij}(r)$ compared with the ionic threshold splittings thus validates a perturbative diagonalization of the $V^{\text{CC}}(r)$ matrix.

An important step in a systematic perturbative diagonalization of this matrix is the inclusion of diagonal elements $V_{ii}(r)$ in the unperturbed Hamiltonian (see the *modified iteration-perturbation* formulas of Morse and Feshbach (1953)). This is immediately apparent when the long-range coupling matrix is written as

$$V_{ij}^{\text{CC}}(r) = \left(\frac{\ell_i(\ell_i + 1)}{2r^2} - \frac{1}{r} + E_i + V_{ii}(r) \right) \delta_{ij} + V_{ij}(r), \quad (10)$$

where the $V_{ij}(r)$ now indicate purely off-diagonal contributions. A spherical multipole expansion of $V_{ij}(r)$ now usefully separates the core-electron and Rydberg-electron coordinates

$$\begin{aligned} V_{ij}(r) &= \sum_{k=0}^{\infty} \langle \phi_i | \frac{r_i^k}{r^{k+1}} P_k(\cos \theta_{ir}) | \phi_j \rangle \\ &= \sum_{k=0}^{\infty} \langle \phi_i | \frac{r_i^k}{r^{k+1}} C^{(k)}(\hat{r}_i) \cdot C^{(k)}(\hat{r}) | \phi_j \rangle, \end{aligned} \quad (11)$$

where the $C^{(k)}$ are renormalized spherical harmonics.

The perturbative diagonalization of the $V^{\text{CC}}(r)$ matrix, through second order in $V_{ij}(r)$, produces terms involving summations over intermediate channels ν with potential energy denominators $U_\mu(r) - U_\nu(r)$. These second-order contributions can be classified as either degenerate or nondegenerate depending on whether or not an intermediate channel ν is degenerate with the physically relevant channel μ at $r \rightarrow \infty$ (i.e., $U_\nu = U_\mu$). The coupling to nondegenerate channels (i.e., $E_\nu \neq E_\mu$) contributes a long-range potential with the structure

$$u_\mu(r) = E_\mu - \frac{1}{r} + \frac{\ell_\mu(\ell_\mu+1)}{2r^2} + \frac{Q_{\mu\mu}^{(2)}}{r^3} - \frac{\alpha_\mu}{2r^4} + \frac{Q_{\mu\mu}^{(4)}}{r^5} + \frac{\beta_\mu^{ad} + \beta_\mu^{nad} - 2(E - E_\mu)\lambda_\mu - \delta_\mu - \eta_\mu}{2r^6} + O\left(\frac{1}{r^8}\right), \quad (12)$$

where *ad* (or *nad*) is our shorthand notation for *radially* adiabatic (or nonadiabatic). (Note that a radially adiabatic term like β_μ^{ad} still includes nonadiabatic coupling in the *angular* degrees of freedom.) Most terms in this potential can be written as a standard second-order perturbation sum. The exceptions include the diagonal quadrupole $Q_{\mu\mu}^{(2)}$ and hexadecapole $Q_{\mu\mu}^{(4)}$ terms which are diagonal (first-order) matrix elements of the ionic electric quadrupole and hexadecapole operators. Also, the term involving the energy-dependent postadiabatic term λ_μ deviates from the normal perturbation expansion, deriving instead from the postadiabatic expansion discussed above. Explicit expressions for these terms as infinite perturbation sums over bound and continuum states of the core, can be obtained along the lines of the derivation given by Watanabe and Greene (1980), although there are differences in notation, in coupling scheme, and in the multipoles that were included. Each term $Q_{\mu\mu}^{(2)}$, $Q_{\mu\mu}^{(4)}$, α_μ , β_μ^{ad} , β_μ^{nad} , λ_μ , δ_μ , and η_μ depends on the various quantum numbers J_μ , ℓ_μ , and K in a relatively complicated fashion that is difficult to analyze:

$$Q_{\mu\nu}^{(k)} = \langle \mu | \sum_{i=1}^{N_c} r_i^k P_k(\cos\theta_{ir}) | \nu \rangle, \quad (13)$$

$$\alpha_\mu = \sum_{\nu \neq \mu} \frac{2Q_{\mu\nu}^{(1)}Q_{\nu\mu}^{(1)}}{E_\nu - E_\mu}, \quad (14)$$

$$\beta_\mu^{ad} = \sum_{\nu \neq \mu} \frac{[\ell_\nu(\ell_\nu+1) - \ell_\mu(\ell_\mu+1)]}{(E_\nu - E_\mu)^2} Q_{\mu\nu}^{(1)}Q_{\nu\mu}^{(1)}, \quad (15)$$

$$\beta_\mu^{nad} = \sum_{\nu \neq \mu} \frac{4Q_{\mu\nu}^{(1)}Q_{\nu\mu}^{(1)}}{(E_\nu - E_\mu)^2}, \quad (16)$$

$$\lambda_\mu = \sum_{\nu \neq \mu} \frac{8Q_{\mu\nu}^{(1)}Q_{\nu\mu}^{(1)}}{(E_\nu - E_\mu)^3}, \quad (17)$$

$$\delta_\mu = \sum_{\nu \neq \mu} \frac{2Q_{\mu\nu}^{(2)}Q_{\nu\mu}^{(2)}}{E_\nu - E_\mu}, \quad (18)$$

and

$$\eta_\mu = \sum_{\nu \neq \mu} \frac{4Q_{\mu\nu}^{(1)}Q_{\nu\mu}^{(3)}}{E_\nu - E_\mu}. \quad (19)$$

In Eq. (13) N_c denotes the number of ionic core electrons, while the subscript r refers to the Rydberg electron. One consequence of including nonadiabatic effects is the appearance of an energy dependent term in the long-range potential. This energy dependence has been difficult to sort out because different treatments disagree

in multiplicative constants (Seaton and Steenman-Clark, 1977; Drachman, 1982). Drachman (1982) shows, however, that the energy dependent term of order $1/r^6$ can be written as an ℓ -dependent linear combination of $1/r^7$ and $1/r^8$, implying that the energy-dependent term can be regarded as a contribution of higher order than $1/r^6$.

E. Degenerate channel contributions

The nature of the long-range potential changes qualitatively when degenerate terms are present. For instance, in the $3pn\ell$ channels of Mg, the $3pnf$ and $3pnh$ channels are degenerate, which results in a very long-range quadrupole coupling between them. Second-order degenerate contributions appear when intermediate channels ν share the same threshold energies $E_\nu = E_\mu$, K -value, and parity with the physically relevant channel μ at $r \rightarrow \infty$. However, for simplicity we assume that (as in the Mg case cited above) the intermediate Rydberg electron orbital momentum ℓ_ν differs from ℓ_μ for all degenerate channels. A derivation similar to that given above produces two additional contributions to the potential $u_\mu(r)$ that originate in coupling to the degenerate channels:

$$\tilde{u}_\mu(r) = u_\mu(r) + \frac{a_\mu}{r^4} + \frac{b_\mu}{r^6} + O\left(\frac{1}{r^8}\right), \quad (20)$$

where the a_μ and b_μ terms are explicitly

$$a_\mu = \sum_{\nu \neq \mu} \frac{2Q_{\mu\nu}^{(2)}Q_{\nu\mu}^{(2)}}{\ell_\mu(\ell_\mu+1) - \ell_\nu(\ell_\nu+1)} \quad (21)$$

and

$$b_\mu = \sum_{\nu \neq \mu} \frac{4Q_{\mu\nu}^{(2)}Q_{\nu\mu}^{(4)}}{\ell_\mu(\ell_\mu+1) - \ell_\nu(\ell_\nu+1)}. \quad (22)$$

Equation (20) excludes one potentially important type of degenerate channel coupling. It arises when two or more ionic states of opposite parity are degenerate and can consequently support a permanent dipole moment: when this occurs, the result is a term proportional to $1/r^2$ at large r . The resulting degenerate dipole coupling of channels can be important, e.g., in the properties of doubly excited states of the hydrogen negative ion. This case must be treated as in Seaton (1961) and Gailitis and Damburg (1963), rather than through the formulas of this paper. After a transformation to the representation in which the long-range dipole coupling is diagonal in such instances, the effects of other (nondipole) multipoles can be handled using the present techniques.

III. RECOUPLING AND PARAMETRIZATION

The long-range anisotropic potential developed in the previous sections involves various terms that depend on the quantum numbers of both the core and the Rydberg electron in a rather complicated way. This complexity intertwines the core properties, such as its multipole moments and polarizabilities, with those of the Rydberg

electron, and somewhat obscures the operator structure of the interaction between the Rydberg electron and the core. To clarify the dependence of each term on J_c , ℓ , and K , and to reveal the operator structure of the full potential, we disentangle each term using Wigner-Racah recoupling algebra and place each into the form

$$\sum_k (-1)^k X^{(k)} \cdot Y^{(k)}, \quad (23)$$

where $X^{(k)}$ operates on the ionic core while $Y^{(k)}$ operates on the Rydberg electron. Next we replace the tensorial structure with coupled unit tensorial operators acting in the space of the core and the Rydberg electron (Clark *et al.*, 1996; Clark and Greene, 1997), respectively. In many systems these unit tensorial operators can be replaced with simpler angular momentum operators of equal rank that generate the same coupling and reflect the basic symmetry properties of the system.

The separation of the core and Rydberg electron operators enables us to perform one last and crucial transformation: the parametrization of the long potential. For each power of $1/r$ there is a channel-dependent coefficient that depends only on properties of the ionic core. These coefficients can be readily identified as the scalar and tensor multipole moments, polarizabilities, and hyperpolarizabilities that characterize the interaction of the core with the Rydberg electron.

In low- Z atomic systems where the spin-orbit interaction is small compared with electrostatic interactions, the total orbital angular momentum L_c and the total spin S_c of the core are approximately good quantum numbers. Regrouping terms with the same r dependence and tensorial structure, the nondegenerate long-range potential, for a low- Z atomic system, leads to the form

$$u_\mu(r) = \frac{\ell_\mu(\ell_\mu+1)}{2r^2} - \frac{1}{r} + E_\mu - \frac{\alpha_s}{2r^4} - \frac{\eta_s}{r^6} - \left(\frac{Q}{r^3} + \frac{\alpha_t}{2r^4} + \frac{\eta_t}{r^6} \right) \mathcal{A}_{\mu\mu}^{(2)} + \frac{\beta_v}{r^6} \langle \vec{L}_c \cdot \vec{\ell} \rangle_{\mu\mu}, \quad (24)$$

which better displays its operator structure and anisotropic nature. The parameters α_s and α_t are the standard scalar and tensor dipole polarizabilities, Q is the quadrupole moment, and η_s and η_t are higher-order scalar and tensor hyperpolarizabilities. Explicit expressions for all terms, including the angular factor $\mathcal{A}_{\mu\mu}^{(2)}$ are given in Clark *et al.* (1996) and Clark and Greene (1997).

The new vector interaction proportional to $\vec{L}_c \cdot \vec{\ell}$ is similar in structure to a term predicted by Zygelman (1990). We also note that a term of this tensorial structure was introduced into atomic spectroscopy by Trees (1951a, 1951b, 1952) and Racah (1952), on semiempirical grounds and without an explicit derivation or formal justification. As a complement and extension of the work of Zygelman, we provide an explicit expression for the coefficient of this unusual interaction and interpret its physical origin. The vector hyperpolarizability β_v is given by

$$\beta_v = \sum_\nu c_\nu \frac{|d_\nu|^2}{(E_\nu - E_{\mu_0})^2}, \quad (25)$$

where d_ν is the reduced matrix element of the core dipole operator

$$d_\nu = \langle \gamma_c L_c \| \sum_{j=1}^{N_c} r_j C^{(1)}(\hat{r}_j) \| \gamma_\nu L_\nu \rangle, \quad (26)$$

and c_ν is the angular coefficient

$$c_\nu = \sqrt{\frac{3}{2}} \frac{1}{\sqrt{L_c(L_c+1)(2L_c+1)}} \begin{Bmatrix} 1 & L_c & L_c \\ L_\nu & 1 & 1 \end{Bmatrix}. \quad (27)$$

The existence of this term has been controversial since a simple parity argument might seem to negate the existence of any odd-rank moments in the long-range potential. The parity argument fails, however, because it is an *even parity pseudovector* in the ionic core degrees of freedom, as we discussed in the Introduction. Nevertheless this term would *still* vanish were it not for the $\ell_\nu(\ell_\nu+1)$ factor inside the summation for β_μ^{ad} (cf. Eq. (15)), which allows the β_v coefficient to survive. To show that terms in the untransformed potential in Eq. (5) without such an additional ℓ_ν dependence cannot generate odd tensorial contributions such as $\vec{L}_c \cdot \vec{\ell}$, we evaluate the summation over ℓ_ν explicitly:

$$\begin{aligned} & \sum_{\ell_\nu} (-1)^{\ell_\nu} (2\ell_\nu+1) \{ \ell_\mu, a, \ell_\nu \} \{ \ell_\nu, b, \ell_\mu \} \\ & \times \begin{Bmatrix} a & b & k \\ \ell_\mu & \ell_\mu & \ell_\nu \end{Bmatrix} = (-1)^{a+b+k} \{ a, b, k \} \{ \ell_\mu, \ell_\mu, k \}. \end{aligned} \quad (28)$$

Here the bracket $\{x, y, z\}$

$$\{x, y, z\} = \begin{pmatrix} x & y & z \\ 0 & 0 & 0 \end{pmatrix} \quad (29)$$

is a condensed notation for 3- j symbols whose magnetic quantum numbers vanish. Since each contribution to our long-range potential involves a and b multipole moments that add up to an even number, by parity, the tensorial rank k must be even in this case.

However, if there is an additional ℓ_ν dependence, such as $\ell_\nu(\ell_\nu+1)$ in β_μ^{ad} , the summation becomes

$$\begin{aligned} & \sum_{\ell_\nu} (-1)^{\ell_\nu} \ell_\nu(\ell_\nu+1) (2\ell_\nu+1) \{ \ell_\mu, 1, \ell_\nu \}^2 \\ & \times \begin{Bmatrix} 1 & 1 & 1 \\ \ell_\mu & \ell_\mu & \ell_\nu \end{Bmatrix} = (-1)^{\ell_\mu+1} \left[\frac{2}{3} \frac{\ell_\mu(\ell_\mu+1)}{(2\ell_\mu+1)} \right]^{1/2}, \end{aligned} \quad (30)$$

which is nonzero for Rydberg states with $\ell_\mu \neq 0$. Thus it is the centrifugal energy of the Rydberg electron, or the angular motion, that generates the vector interaction.

An identical analysis can be applied to the degenerate contributions of the long-range potential. The degenerate coefficients depend on permanent quadrupole

and/or hexadecapole moments of the ionic core, but like the vector hyperpolarizability, they also depend on the orbital momentum of the Rydberg electron. For these reasons the degenerate contributions are generally small, but cannot be neglected if a single channel adiabatic analysis is used to interpret experimental Rydberg energy distributions.

In order to preserve the simple structure of the non-degenerate long-range potential and to describe Rydberg state energies in systems where channel coupling can be important, a *diabatic* variant of the above formulation can be helpful for practical calculations. This diabatic reformulation involves a perturbative expansion of a Green's function, in contrast to the above perturbative diagonalization of an adiabatic Hamiltonian. The diabatic treatment produces an effective Hamiltonian with a potential matrix that approximately resembles the non-degenerate long-range potential, while allowing for coupling between different μ and μ' channels:

$$H_{\mu\mu'} = -\frac{1}{2} \frac{d^2}{dr^2} + \frac{\ell_\mu(\ell_\mu+1)}{2r^2} - \frac{1}{r} + E_\mu - \frac{\alpha_s}{2r^4} - \frac{\eta_s}{r^6} - \left(\frac{Q}{r^3} + \frac{\alpha_i}{2r^4} + \frac{\eta_i}{r^6} \right) \mathcal{A}_{\mu\mu'}^{(2)} + \frac{\beta_v}{r^6} \langle \vec{L}_c \cdot \vec{\ell} \rangle_{\mu\mu'}. \quad (31)$$

The appearance of degenerate contributions within the adiabatic approximation reflects the manner in which this theoretical formulation attempts to incorporate the coupling of degenerate channels. However, since the adiabatic approximation generally stresses qualitative and physical insight rather than spectroscopic accuracy of the resulting level spectrum, we advocate bypassing the complexity of an adiabatic analysis in most cases. This can be done with relative ease through a diabatic formulation of the coupling among degenerate or nearly degenerate channels developed by Clark *et al.* (1996).

IV. QUALITATIVE INTERPRETATION OF THE VECTOR INTERACTION TERM

One of the greatest challenges faced in our analysis is to develop a qualitative interpretation of the vector interaction term. We address this in the present section from different points of view: first through an analytical rearrangement of the operator structure, and then through a two-electron example that we consider from both a classical viewpoint and a quantum mechanical viewpoint.

A. Analysis using recoupling methods

First we show how the form of the interaction term can be recast into an analytical form in which a cross product of the core electric dipole operators appears as a projection onto the orbital angular momentum of the Rydberg electron. Such a cross product is suggestive of the presence of torques in the nonadiabatic electron-core interaction dynamics, as is the occurrence of

pseudovectors in the interaction term, for that matter. In order to see how torques arise in the electric dipole interaction term between the Rydberg electron and the core, we begin by rewriting β_μ^{ad} as

$$\beta_\mu^{ad} = \sum_{v \neq \mu} \frac{[\ell_v(\ell_v+1) - \ell_\mu(\ell_\mu+1)]}{(E_v - E_\mu)^2} Q_{\mu v}^{(1)} Q_{v\mu}^{(1)} = \sum_{v \neq \mu} \frac{\langle \mu | [\hat{r}, \vec{\ell}^2] \cdot \vec{r}_v | v \rangle \langle v | \hat{r}' \cdot \vec{r}_c' | \mu \rangle}{(E_v - E_\mu)^2}. \quad (32)$$

The variables in the second matrix element in the preceding equation are primed, to serve as a reminder that they are integrated over independently of the variables in the first matrix element. The commutator of \hat{r} and $\vec{\ell}^2$ is

$$[\hat{r}, \vec{\ell}^2] = i(\vec{\ell} \times \hat{r} - \hat{r} \times \vec{\ell}), \quad (33)$$

and with a little recoupling, the term of vectorial nature in β_μ^{ad} is seen to be proportional to

$$([\hat{r}, \vec{\ell}^2] \times P\hat{r}') \cdot (\vec{r}_c \times P_c \vec{r}_c'). \quad (34)$$

Using

$$[\hat{r}, \vec{\ell}^2] \times P\hat{r}' = -2i(\hat{r} \cdot P\hat{r}')\vec{\ell} + 2i\hat{r}(\vec{\ell} \cdot P\hat{r}') - 2\hat{r} \times P\hat{r}' \quad (35)$$

we see the emergence of a $1/r^6$ vector interaction term proportional to

$$\sim \vec{\ell} \cdot (\vec{r}_c \times P_c \vec{r}_c'). \quad (36)$$

The existence of this vector interaction hinges on the presence of the centrifugal $\ell(\ell+1)$ factors in the expression for β_μ^{ad} , which again supports our interpretation that the interaction results from the angular motion of the Rydberg electron. Moreover, the vector cross product on the right-hand side of Eq. (33) suggests that the Rydberg electron exerts a torque on the ionic core, when the motion of the Rydberg electron tries to “drag” the polarization vector of the spinning ionic core.

B. A two-electron example treated classically

Next we return to the example discussed in Fig. 1, with two nonoverlapping coplanar electrons that move in the field of a bare charge $Z=2$ nucleus. The inner electron is initially in a circular Bohr orbit with $n_1=2$ and $\ell_1=1$, while the outer electron is started in a circular orbit with $n_2=7$ and $\ell_2=6$. The zeroth-order Hamiltonian for this system then looks like

$$H_0 = \frac{1}{2} \vec{p}_1^2 + \frac{1}{2} \vec{p}_2^2 - \frac{2}{r_1} - \frac{1}{r_2}. \quad (37)$$

We have assumed here that $r_2 \gg r_1$, whereby the inner electron ($r_1 \approx 2$) fully screens the outer electron ($r_2 \approx 49$), and the leading order perturbation to H_0 is the dipole component of the electron-electron interaction:

$$V = \frac{r_1 \cos \theta_{12}}{r_2^2}. \quad (38)$$

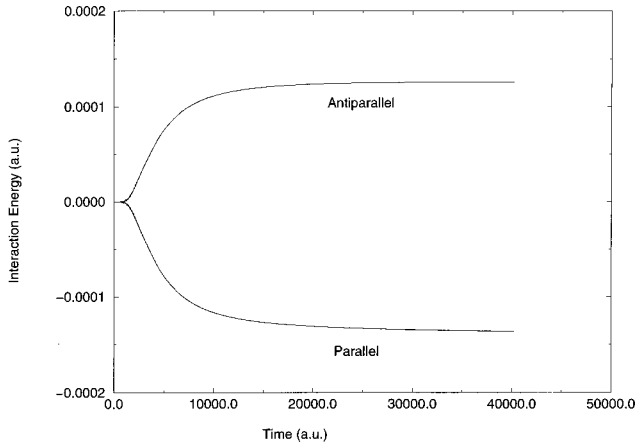


FIG. 3. The classical energy shift versus time for the model discussed in Sec. IV.B, consisting of an inner “ $2p$ ” electron and an outer “ $n=7, \ell=6$ ” electron. The dipole interaction is “ramped on” over several orbital periods of the outer electron. The unperturbed orbits are initially circular and coplanar, with the two angular momenta parallel in the lower curve and antiparallel in the upper curve. After the “ramp function” saturates for $t \approx 10^4$ a.u., the energy shifts become constant and can be viewed as the classical analogs of a perturbative quantal energy shift (see text).

In order to find the energy shift of the system due to the perturbative dipole interaction V , we have propagated classical trajectories for the Hamiltonian $H_0 + R(t)V$, where $R(t)$ is an adiabatic “ramp-on” that is zero at time $t=0$ and becomes unity after many orbit periods of the outer electron. (This method of evaluating perturbation energies in conjunction with classical mechanics was used successfully in a different context by Hooker *et al.* (1997).) Figure 3 shows that the resulting perturbation in the energy of the system has opposite sign for the two geometries of Fig. 1. In particular, the energy shift is negative when the two angular momenta $\vec{\ell}_1$ and $\vec{\ell}_2$ are parallel (left-hand case in Fig. 1), while the energy shift has nearly the same magnitude but is positive when these angular momenta are antiparallel (right-hand case in Fig. 1).

C. Two-electron example treated using quantum mechanics

The same system just considered classically possesses a simple quantal description. One quantitative difference between this example of a one-electron ionic core in the $n_1=2$ state of He^+ and the cases formulated in Secs. II and III, is that a one-electron hydrogenic ion possesses the unusual “accidental degeneracy” (when fine structure is neglected) of the $2s$ and $2p$ substates. It is well known that this degeneracy magnifies the effect of the dipole interaction between a distant electron and the hydrogenic ion, which is one reason we have chosen this example. At the same time, this system can be treated simply using 2 by 2 matrices in an LS -coupled representation. In the following, we let r stand for r_2 , the distance of the outer electron from the nucleus,

while ℓ is the orbital angular momentum of that outer electron. The leading order term at $r \rightarrow \infty$ in the potential accordingly contributes in order r^{-2} , i.e., on a par with the centrifugal term in the Rydberg electron Hamiltonian.

The quantum mechanical channel describing this $2pn\ell$ two electron atom thus has the following character. When the angular momenta of the inner ($\ell_1=1$) and outer electron ($\ell=6$) are “parallel,” the zeroth-order state can be written as $|(2p, n\ell=6)L=7\rangle$, i.e., as an eigenstate of $\vec{L}^2 = L(L+1)$ with $L=7$. The dominant channel that couples to this state is the channel $|(2s, n\ell+1=7)L=7\rangle$. The correction to the long-range Coulomb potential of the outermost electron is therefore a dipolar $\propto 1/r^2$ potential for this example, whose coefficient is obtained by diagonalization of the combined centrifugal and dipole-interaction potentials. Through dipolar order, neglecting terms of order r^{-3} , the effective potential appropriate for parallel angular momenta is the smaller eigenvalue of

$$V^{\text{eff}}(r) = -\frac{1}{r} + \begin{pmatrix} \frac{\ell(\ell+1)}{2r^2} & \frac{d}{r^2} \\ \frac{d}{r^2} & \frac{(\ell+1)(\ell+2)}{2r^2} \end{pmatrix}.$$

Here d is a matrix element of the core electric dipole operator between the two coupled channels, $d = \langle 2p | r_1 | 2s \rangle \langle (1\ell)L=\ell+1 | \cos\theta_{12} | (0, \ell+1)L=\ell+1 \rangle = -\sqrt{21/20}$. The analogous effective potential relevant for antiparallel angular momenta of the core and the Rydberg electron is the larger eigenvalue of

$$V^{\text{eff}}(r) = -\frac{1}{r} + \begin{pmatrix} \frac{\ell(\ell+1)}{2r^2} & \frac{d'}{r^2} \\ \frac{d'}{r^2} & \frac{(\ell-1)\ell}{2r^2} \end{pmatrix},$$

where $d' = \langle 2p | r_1 | 2s \rangle \langle (1\ell)L=\ell-1 | \cos\theta_{12} | (0, \ell-1)L=\ell-1 \rangle = \sqrt{27/22}$. The resulting eigenvalues give effective potentials for the outer ($\ell=6$) electron:

$$V_{\uparrow\uparrow}^{\text{eff}}(r) = -\frac{1}{r} + \frac{\ell(\ell+1)}{2r^2} - \frac{0.147}{r^2},$$

$$V_{\uparrow\downarrow}^{\text{eff}}(r) = -\frac{1}{r} + \frac{\ell(\ell+1)}{2r^2} + \frac{0.198}{r^2}.$$

The last term in each potential gives the effect of the perturbation. The quantum mechanical estimate of the perturbation energy is obtained by averaging the last term in the above two potentials over the radial $n=7$, $\ell=6$ orbital, which gives: $\Delta_{\uparrow\uparrow}^{QM} = -6.6 \times 10^{-5}$ a.u., and $\Delta_{\uparrow\downarrow}^{QM} = 8.9 \times 10^{-5}$ a.u. These quantum mechanical energy shifts for this example are within about a factor of two of the classically estimated energy shifts, confirming that the basic classical picture presented above is qualitatively correct. Interestingly, the quantum mechanical

interpretation for this prototype two-electron example shows that the different sign of the energy perturbation for parallel and antiparallel angular momenta is a consequence of differential level repulsion. The state $2pn/[L=\ell+1]$, with parallel angular momenta, is pushed down in energy by its interaction with the higher-lying $2sn'(\ell+1)[L=\ell+1]$ state, whereas the state $2pn/[L=\ell-1]$, with antiparallel angular momenta, is pushed up in energy by the lower $2sn'(\ell-1)[L=\ell-1]$ state. This qualitative interpretation remains similar when the ionic s and p levels are not degenerate, except that the differential level repulsion then causes the ℓ dependence in the potential to begin at the r^{-6} level rather than the r^{-2} level.

V. NON-ABELIAN GAUGE FORMULATION

Zygelman (1990) was the first to predict the existence of the vector interaction and to estimate the magnitude of the proportionality constant. In an original and pioneering approach, he used ideas of non-Abelian gauge fields and geometric phases to study long range atomic forces. Extending the work of Berry (1984), Wilczek and Zee (1984), Jakiw (1986), and Moody *et al.* (1986), he realized that the derivative coupling matrix within an adiabatic representation resembles a vector potential or a non-Abelian gauge field, an artifact of the representation. As with minimal coupling, a gauge transformation can in principle be found that eliminates the vector potential. However, if the channel space is finite or truncated the derivative coupling can only approximately be removed by a gauge transformation, leaving an effective potential, as in our formulation. It was based on this framework that Zygelman first suggested that a vector interaction involving $\vec{L}_c \cdot \vec{\mathcal{L}}$ should be present in the long-range interaction between a charged particle and an anisotropic system.

VI. RYDBERG STATES OF NEON

The importance of the vector interaction and the channel coupling provided by the effective Hamiltonian approach have been demonstrated for the $n=10$ Rydberg states of Ne with orbital momenta $\ell=5, 6, 7$, and 8 . These states were studied in recent experiments by Ward *et al.* (1996), with the full interpretation emerging from our theoretical analysis (Clark *et al.*, 1996; Clark and Greene, 1997; Clark, 1998). Most importantly, for the purposes of this paper, this example permits a detailed test of the capability of our parametrized long-range potential to describe the Rydberg state energy levels that are attached to the lowest ionization threshold. The theoretical computation of Rydberg energies was accomplished by diagonalization of the Hamiltonian in Eq. (31), followed by a minimization of the weighted χ^2 function (involving differences between the observed and computed energy levels) with respect to the parameters $\alpha_s, \alpha_t, \beta_v, \dots$. It is worth noting that there is nothing *ad hoc* about the parametrized theory. Analytic

expressions for each parameter are given in our previous publications, and each can be computed from first principles. In fact, an *ab initio* calculation of $\alpha_s, \alpha_t, \beta_v, \dots$ using multiconfiguration Hartree-Fock atomic wave functions was a key component of the proposed theoretical interpretation.

The experimentally observed spin splittings were only partially resolved in the Ward *et al.* (1996) experiment; these were analyzed by the experimental group to extract “spinless” transition frequencies. We neglected all spin-orbit terms in the Rydberg electron Hamiltonian, and all exchange interactions between a core electron and the Rydberg electron. The dominant perturbative effects (in addition to those described above) that must be added to our computed Rydberg levels are mass polarization (i.e., arising from the small deviation of the atomic center of mass from the nuclear center of mass) and the magnetic interaction between the Rydberg electron and the ionic core, given by

$$H_{\text{mag}} = -\frac{g_J}{2} \alpha^2 \frac{\vec{J}_c \cdot \vec{\mathcal{L}}}{r^3}, \quad (39)$$

where α is the fine-structure constant and g_J is the g factor of the ionic core.

The results of our analysis are summarized in Tables I and II. Table I compares the various fitted parameters for Ne^+ with those obtained in a fit carried out by Ward *et al.* (1996). Our own fitted results improve the χ^2 by some 80% over the χ^2 obtained in the fit carried out by Ward *et al.* (1996). The fact that our χ^2 per degree of freedom (per parameter) is now approximately 1 suggests that our anisotropic Hamiltonian correctly accounts for the energetics of these Rydberg levels. It also suggests that our nonperturbative calculation of the Rydberg electron radial motion within the coupled channels improves somewhat upon the perturbative description of the radial motion adopted by Ward *et al.* Our computed levels are compared in Table II with those of Ward *et al.* (1996), for the $n=10$ Rydberg states of Ne with $\ell=5, 6, 7$, and 8 . These parameters reproduce all observed energy level splittings to 500 kHz or better.

In order to determine the importance of the vector interaction term in our long-range Hamiltonian, we have repeated the same least-squares fitting analysis that was described in the preceding paragraph, except the vector hyperpolarizability β_v was constrained to vanish. Table I lists the fitted parameters obtained from this analysis with β_v omitted. The greatest change among the parameters occurs in the fitted $\text{Ne}^+ \ ^2P_{3/2}$ gyromagnetic ratio g_J , which changes from 1.342 to 1.307. The tensorial structure of the gyromagnetic term is similar to that of the vector interaction and it is not surprising that the resulting fit modifies g_J to “mock up” the effects omitted by setting β_v equal to zero. Since the ℓ dependence of the spin-orbit interaction is very different from that of the term involving β_v , however, a change in g_J can only crudely compensate for the omission of β_v from the fit. Note also that the LS coupling value of g_J is precisely $4/3$, but spin-orbit interactions in the Ne^+ ion can

TABLE I. Comparison of fitted (experimental) and theoretical parameters for Ne^+ . L refers to length form and V refers to velocity form. The value of g_J in column 4 is based on pure LS coupling. The values labeled “present” are from our earlier work (Clark, *et al.*, 1996), as are the unlabeled theoretical values for α_s , α_t , and β_v . (The errors quoted for the fitted parameters in the first two columns are probably underestimated. The authors thank S. R. Lundeen for pointing out a study by Komara *et al.* (1998) which discusses this point.)

	Present fit	Present fit without β_v	Ward <i>et al.</i>	Theoretical
Q	-0.204020(5)	-0.204001(11)	-0.20403(5)	-0.1964 (Sundholm and Olsen, 1994) -0.2032(5) (Sundholm and Olsen, 1994) -0.2117 (Ward <i>et al.</i> , 1996)
α_s	1.3018(2)	1.3011(6)	1.3028(13)	1.23 (L) 1.19 (V) 1.27 (Hibbert <i>et al.</i> , 1977)
α_t	-0.0259(3)	-0.0261(3)	-0.026(5)	-0.0374 (L) -0.0396 (V) -0.035 (Ward <i>et al.</i> , 1996)
β_v	0.059(2)	“0”	0.045(29)	0.0678 (L) 0.0719 (V)
η_s	-0.10(1)	-0.10(1)	-0.29(24)	-1.44 (Chang <i>et al.</i> , 1994)
η_t	0.274(5)	0.264(3)	0.5(5)	
g_J	1.342(12)	1.307(24)	1.354(21)	4/3
χ^2	7.1	27.5	35.7	

TABLE II. Comparison of calculated (with and without β_v , see Clark *et al.* (1996)) and experimentally observed (Ward *et al.*, 1996) energies (MHz) of $n=10$ Rydberg neon with $J_\mu=3/2$ and $\ell=5, 6, 7$, and 8. $\Delta E = E_{\text{obs}} - E_{\text{calc}}$.

States	E_{obs} (MHz)	E_{calc}	ΔE	$E_{\text{calc}}^{\beta_v=0}$	$\Delta E^{\beta_v=0}$
$H_{9/2}$	-145.58(77)	-145.63	0.05	-144.15	-1.43
$H_{11/2}$	2142.67(10)	2142.60	0.07	2142.81	-0.14
$H_{13/2}$	-6022.24(19)	-6022.02	0.22	-6022.66	0.42
$I_{9/2}$	-5267.15(35)	-5267.38	0.23	-5266.64	-0.51
$I_{11/2}$	-356.30(24)	-356.18	-0.12	-355.91	-0.39
$I_{13/2}$	800.52(5)	800.50	0.02	800.55	-0.03
$I_{15/2}$	-4131.36(15)	-4131.35	-0.01	-4131.10	-0.26
$K_{11/2}$	-3838.06(35)	-3838.50	0.44	-3838.26	0.20
$K_{13/2}$	-646.41(8)	-646.37	-0.04	-646.36	-0.05
$K_{15/2}$	“0”	“0”	“0”	“0”	“0”
$K_{17/2}$	-3205.01(16)	-3204.97	-0.04	-3204.68	-0.33
$L_{13/2}$	-3073.14(35)	-3073.64	0.50	-3073.56	0.42
$L_{15/2}$	-883.09(8)	-883.04	-0.05	-883.08	-0.01
$L_{17/2}$	-494.04(5)	-494.04	0.00	-494.05	0.01
$L_{19/2}$	-2693.41(18)	-2693.38	-0.03	-2693.14	-0.27

change this value from its LS -coupled limiting value. (A separate measurement of the ionic linear Zeeman effect could in principle test our fitted g_J value independently.)

The computed Rydberg levels we obtain with the vector interaction *omitted* are also given in Table II. The largest discrepancies between the computed and observed levels appear in the lower ℓ states, where the largest difference is -1.43 MHz for the $n=10$ $H_{9/2}$ state. Most important is the clear degradation in the quality of the fit when we constrain $\beta_v=0$. The new least-squares fit obtained with $\beta_v=0$ results in $\chi^2=27.5$, approximately four times worse (per degree of freedom) than the fit including the vector interaction. We interpret this as evidence that the existence of the vector interaction has been confirmed by the Ward *et al.* (1996) measurement of Rydberg states of Ne.

To complement our analysis of this Rydberg system, Table I compares our separately calculated *ab initio* theoretical values for α_s , α_t , and β_v with other theoretical and experimental results. (These are obtained using both the length and velocity forms of the electric dipole matrix elements, which should agree if the ionic wave functions are exact.) The details of these calculations are presented by Clark *et al.* (1996). In view of the difficulty of the *ab initio* calculation of such parameters for the many-electron ion Ne^+ , the calculated values are seen to agree reasonably well with the values deduced from our fit to the measurements of Ward *et al.* (1996). This strengthens the argument that the vector interaction does exist and plays an important role in certain features of Rydberg spectra.

VII. SUMMARY AND CONCLUSIONS

Our interest in this subject originated with the prediction, by Zygelman (1990), of a nonrelativistic “orbit-orbit-type” potential in Rydberg systems with non-spherical cores. The use of standard atomic and molecular theory techniques has established the existence and provided some degree of understanding of the physical origin of such an interaction. Moreover, this analysis has spawned an improved theory that permits a spectroscopically accurate description of Rydberg electron motion in the field of an arbitrary anisotropic core.

This unusual potential, purely electrostatic in nature despite the vector structure, exists because of three effects: the dipole interaction between the core and the Rydberg electron, the angular motion of the Rydberg electron, and the anisotropy of the core with nonzero angular momentum. Our preliminary analysis seems to indicate that the Rydberg electron exerts a torque on the ionic core, when the motion of the Rydberg electron attempts to “drag” the core polarization vector. This classical notion cannot be developed very far, however, since the dynamics of the ionic core occur at far shorter time scales than the time scale of the Rydberg electron motion, because the ionic core energy splittings are very large ($\Delta E \gg 1$ eV) and also because the ionic properties unavoidably require a quantal description.

Despite the substantial theoretical and experimental interest in high-precision Rydberg state spectroscopy over the years, the vector interaction term of Eq. (1) was not previously identified. A line of research with possibly related insights is that of Berry and Robbins (1993). These authors use classical mechanics to treat a slow massive particle in the field of a fast system with spin \vec{S} , and obtain terms in the interaction that involve \vec{S} and the orbital angular momentum. The quantum mechanical description presented in this paper differs sufficiently in spirit, however, that it has not proven easy to connect it with those other notions, which were termed “geometrical magnetism” by Berry and Robbins (1993).

The study of the $n=10$ Rydberg states of Ne has been the first opportunity to establish the existence of the vector interaction within a Rydberg system. The extraction of the Ne^+ multipole moments, polarizabilities, and hyperpolarizabilities, through a procedure of minimizing a weighted χ^2 function, involving differences between the observed (Ward *et al.*, 1996) and computed energy levels, demonstrated the importance of channel coupling even in high- ℓ states that can usually be described by perturbative methods. The 80% reduction in the χ^2 per degree of freedom is evidence for the importance of the vector interaction. Moreover, the approximate agreement between the fitted coefficient and our relatively crude calculation of the vector hyperpolarizability (Clark *et al.*, 1996) provides further confirmation of this surprising vector interaction.

While almost any Rydberg system with an anisotropic core offers the opportunity to gain more insight into the vector and other anisotropic interactions, the most promising systems are simple diatomic systems like H_2 , D_2 , and HD where accurate core wave function information can be obtained. A recent analysis shows that the vector hyperpolarizability β_v for H_2 and D_2 Rydberg states (Clark, 1998) is far smaller than for an atomic ion, owing to the greater rotational inertia of a molecular ion. The additional complexity in the rotational and vibrational degrees of freedom offers fertile possibilities to further our understanding of subtle interactions in quantum physics and to strengthen the fruitful interaction of theory and experiment.

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