

Nonadiabatic long-range forces

A. Dalgarno and P. Shorer*

Harvard-Smithsonian Center for Astrophysics, Cambridge, Massachusetts 02138

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The dependence of the long-range interactions between a Rydberg electron and an ionic core on the nuclear charge of the core is analyzed. It is pointed out that the nonadiabatic interaction will be most readily apparent in spectral-line measurements of systems belonging to the beryllium and boron isoelectronic sequences. A quantitative analysis is presented of data for Cl_{XIV} .

I. INTRODUCTION

A point charge located a large distance r from a charge distribution moves under the action of forces which include, in addition to static spin-orbit, multipole, polarization, and retardation forces, a dynamical force arising from the motion of the point charge. The dynamical potential term, which corresponds to a repulsive force, decreases as r^{-6} ,¹ as does the attractive static quadrupole polarization term.

Some experimental evidence in support of the reality of the dynamical contribution has been discussed by Freeman and Kleppner,² who analyzed data on the energy levels of high Rydberg states of sodium and derived empirically an effective quadrupole polarizability of $0.48a_0^5$, which is considerably smaller than the theoretical value³ of about $1.5a_0^5$ for the quadrupole polarizability of the Na^+ core. We wish to point out that in certain atomic systems the dynamical contribution can be substantially enhanced compared to the other long-range terms, and that for such systems it will modify significantly the energies of the Rydberg levels.

II. THEORY

Consider a spherically symmetric ionic core so that the spin-orbit and electric quadrupole interaction terms vanish. The retardation terms⁴ are usually not significant, and the long-range interaction potential of an electron moving in the field of the ionic core is given by¹

$$W(r) = \frac{-\zeta e^2}{r} - \frac{1}{2} \alpha_d \frac{e^2}{r^4} - \frac{1}{2} (\alpha_q - 6\beta) \frac{e^2}{r^6} + O(r^{-7}),$$

where ζ is the excess charge of the core, α_d is the dipole polarizability of the core, α_q is the quadrupole polarizability, and β characterizes the dynamical contribution.

For a Rydberg electron with quantum numbers nl , described by the orbital $\phi_{nl}(\vec{r})$, the energy level is shifted in response to $W(r)$ by approxi-

mately $\langle \phi_{nl}(\vec{r}) | W(r) | \phi_{nl}(\vec{r}) \rangle$. Because of changes in the functional forms of the individual terms of $W(r)$ and because of exchange effects which are nonlocal, it is necessary to introduce cutoff lengths into $W(r)$ if a significant contribution to the energy shift comes from small values of r .

There occurs also a shift due to penetration of the core, which, if we ignore exchange effects, may be written as

$$W_p = \sum_c \left\langle \left\langle \phi_c(\vec{r}') \phi_{nl}(\vec{r}) \right. \right. \\ \left. \left. \times \left| \frac{-e^2}{r} + \frac{e^2}{|\vec{r} - \vec{r}'|} \right| \phi_c(\vec{r}') \phi_{nl}(\vec{r}) \right\rangle \right\rangle,$$

where the summation is taken over all the core orbitals $\phi_c(\vec{r}')$. The penetration term decreases rapidly with increasing azimuthal quantum number l .

We consider now the variation of the individual terms along an isoelectronic sequence. The penetration contribution increases for large nuclear charges Z as Z . For most systems the dipole polarizability α_d decreases as Z^{-4} , and the quadrupole polarizability α_q and dynamical repulsion β decrease as Z^{-6} . Because the expectation values r^{-4} and r^{-6} increase asymptotically as, respectively, Z^4 and Z^6 , the individual long-range contributions to the energy shift remain in much the same proportion to each other but decrease relative to the penetration correction.

However, for interactions with ionic cores of the lithium $1s^2 2s^2 S$ sequence and the beryllium $1s^2 2s^2 S$ sequence, the degenerate $n=2$ levels are coupled by the dipole interaction so that the dipole polarizability decreases as Z^{-3} ,⁵ the β coefficient decreases as Z^{-4} , and the quadrupole polarizability decreases as Z^{-6} . Thus the energy shift due to dipole polarization increases as Z , the energy shift due to quadrupole polarization tends to a constant, and the energy shift due to the dynamical term increases as Z^2 .

For the Z dependencies of the dipole polarization, quadrupole polarization, and dynamical correlation energies of sequences throughout the

periodic table for which there are intrashell dipole and quadrupole transitions, the relationship is $Z : Z : Z^2$.

For sufficiently large Z these conclusions are modified by relativistic effects which remove the degeneracies.

Our analysis of the Z dependencies suggests that the dynamical effect will emerge most clearly in a study of energy levels of the Rydberg states of berylliumlike and boronlike ions, preferably as functions of nuclear charge. The interpretation of the boronlike system must also take into account the degeneracy of the $1s^2s^2^1S$ and $1s^2p^2^1S$ core configurations.

III. APPLICATIONS TO CLXIV

Accurate wavelengths of transitions involving Rydberg states of the berylliumlike system CLXIV have been measured recently.⁶ For the $5g$ - $6h$ transition the measured frequency is $263\,310 \pm 55 \text{ cm}^{-1}$.⁷ The relativistic energy levels of a hydrogenic atom of charge 14 and mass equal to that of ^{35}Cl are $-860\,507$, $-860\,417$, $-595\,527$, and $-597\,493 \text{ cm}^{-1}$ for the $5g_{7/2}$, $5g_{9/2}$, $6h_{9/2}$, and $6h_{11/2}$ levels, respectively, which yields, upon averaging, a hydrogenic $5g$ - $6h$ transition frequency of $262\,948 \text{ cm}^{-1}$. Thus there is a difference of approximately 362 cm^{-1} between the measured transition frequency and the hydrogenic value.

The penetration contribution W_p , which we have calculated using a Dirac-Hartree-Fock representation of the core orbitals,⁸ is 16 cm^{-1} . We attempt to explain the remaining difference of 346 cm^{-1} as a shift due to the long-range interactions.

The dipole polarizability of the lithiumlike core has been evaluated as a function of the nuclear charge by Cohen,⁹ who gives the nonrelativistic formula

$$\alpha_d(Z) = \frac{254.5}{(Z - 1.182)^3} \alpha_0^3.$$

Most of the polarizability arises from the $1s^2s^2^2S - 1s^2p^2^2P$ transition. Adjusting α_d to reflect relativistic effects which modify the oscillator strengths and split the 2P terms, we estimate a dipole polarizability for the CLXIV core of $0.0659\alpha_0^3$.

We terminate the dipole interaction at a value of r , beyond which the probability of finding the $2s$ electron is small. Appropriate values of the cutoff are in the range 0.5 - $1.1\alpha_0$. With a cutoff of 0.8 a.u. the dipole polarizability contribution to the transition frequency is 892 cm^{-1} . For cutoffs at 0.5 and $1.1\alpha_0$ the contribution is 1088 and 553 cm^{-1} , respectively.

With the cutoff at 0.8 a.u. there remains a shift

of -546 cm^{-1} . The contribution to the transition frequency arising from the attractive quadrupole polarization is positive and increases the difference between the measured and theoretical values. We are therefore led to attribute the difference to the contribution from the repulsive dynamical correlation. Using oscillator strengths from the tabulation of Martin and Wiese,¹⁰ we obtain a value of $0.0286\alpha_0^5$ for the dynamical coefficient. For the quadrupole polarizability we estimate $\alpha_q = 0.001\alpha_0^5$ by extrapolating the calculations of Langhoff *et al.*¹¹ and of Easa and Shukla.¹² Compared to 6β , the quadrupole polarizability is negligible.

The energy shift due to the dynamical term, with a cutoff at 0.8 a.u. , for the r^{-6} interaction is -1791 cm^{-1} . The resulting shift is too large, but a different choice of cutoff for the r^{-6} interaction leads to a net shift of the correct magnitude. Cutoffs of 0.76 a.u. for the r^{-4} interaction and 1.20 a.u. for the r^{-6} interaction provide a shift of the hydrogenic value, adjusted for penetration, which reproduces the experimental transition frequency for the $5g$ - $6h$ transition.

The same choice of cutoffs also reproduces the measured $5f$ - $6g$ transition frequency of $264\,375 \pm 57 \text{ cm}^{-1}$.⁷ The hydrogenic $5f_{5/2}$, $5f_{7/2}$, $6g_{7/2}$, and $6g_{9/2}$ levels are $-860\,657$, $-860\,507$, $-597\,579$, and $-597\,527 \text{ cm}^{-1}$, respectively, leading to an average hydrogenic $5f$ - $6g$ transition frequency of $263\,021 \text{ cm}^{-1}$. The difference of 1354 cm^{-1} between the measured transition frequency and the average hydrogenic value can roughly be attributed to a penetration contribution of 475 cm^{-1} , a dipole polarization contribution of 716 cm^{-1} , and a dynamical contribution of 172 cm^{-1} .

Because of the sensitivity of the $n = 5$ - 6 transition energies to the cutoffs, the quantitative results for the $n = 5$ - 6 transitions may not be highly accurate. However, our qualitative conclusion, that dynamical repulsion is a significant effect, does not depend on the specific numerical examples.

The model we have used should improve in reliability as the principal quantum number of the Rydberg electron increases, since the regions of contribution to the r^{-4} and r^{-6} interactions shift toward larger r , thereby diminishing the dependence of the terms on the cutoff. However, as n increases, the magnitude of $\langle r^{-4} \rangle$ and especially of $\langle r^{-6} \rangle$ decreases, so that the shifts due to the dipole polarizability and the dynamical repulsion become less significant.

For CLXIV, the $7i$ - $8k$ transition provides a balance between these competing factors. For this transition the hydrogenic frequency is $102\,890 \text{ cm}^{-1}$. Including the shift due to the dipole

polarization gives a frequency of $102\,943\text{ cm}^{-1}$; and including the dipole polarization and the dynamical term gives a frequency of $102\,915\text{ cm}^{-1}$.

Measurements of the frequencies for transitions such as the $7i-8k$ transition, which are little affected by penetration and are insensitive to the cutoff, and particularly measurements at other values of the nuclear charge would be valuable in assessing the validity of the model used here

and establishing the significance of the dynamical repulsion term.

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