

Rydberg States of Lithium and Other Systems

The interesting calculation of retardation corrections to excited atomic state energies is facilitated by the existence of good calculations of the nonrelativistic and nonretarded energies, to which retardation corrections can be added. Here I describe a perturbation method, applicable when the angular momentum is high enough, which generates an asymptotic series for the energy. It makes use of generalized polarizabilities of the atomic or ionic core (numerically obtained) but otherwise is completely analytic. It is applied here to the lithium atom in detail, and its application to hydrogen molecular ions is outlined.

Key Words: *Rydberg states, perturbation theory.*

I. INTRODUCTION

An important discussion component of this Topical Group meeting is the interaction of a highly excited single atomic electron with the remaining core electrons when retardation effects are important. Such a Rydberg state can be investigated by measuring the deviations of fine-structure levels from their unperturbed, hydrogenic values; surprisingly high precision has already been achieved in helium [1] and lithium [2] atoms. To carry out the theoretical analysis of these states it is still necessary to obtain a good solution of the nonretarded problem, to which the retardation corrections can be added. Drake [3] has perfected a variational method for finding accurate energies of such states, and his results are definitive, at least for the lower-lying levels. I will give a brief summary here of another method that has been used; it has the advantages of being largely analytic rather than numerical and of improving as the Rydberg electron moves further from the core.

Consider the lithium atom, with two electrons in a $1s^2\ ^1S_0$ core state and the third electron in a highly excited state with quantum numbers (N,L) , described [4] by the following nonrelativistic

Hamiltonian ($Z=3$ for lithium):

$$H_{NR} = \left[-\nabla_1^2 - \nabla_2^2 - \frac{2Z}{r_1} - \frac{2Z}{r_2} + \frac{2}{r_{12}} \right] + \left[-\nabla_x^2 - \frac{2(Z-2)}{x} \right] + \left\{ -\frac{4}{x} + \frac{2}{|\vec{x}-\vec{r}_1|} + \frac{2}{|\vec{x}-\vec{r}_2|} \right\} \quad (1)$$

The first bracket is the Hamiltonian of the core, $H_0(12)$, the second of the Rydberg electron, $H_0(x)$ and the braces contain the interaction between the two parts, H_{int} , which decreases rapidly with increasing distance of the third electron, x . To a pretty good approximation, the energy of this system is $\epsilon_0 - 1/N^2$, where ϵ_0 is the energy of the core, and the third electron moves in an almost pure Coulomb potential, $2/3$ shielded by the core. Our problem is to find the small, L -dependent corrections to this zero-order energy.

II. THE METHOD

We first expand the interaction in a multipole series, with $x \gg r_{1,2}$:

$$H_{int} = \sum_{l=1}^{\infty} \sum_{j=1}^2 \frac{2r_j^l}{x^{l+1}} P_l(\hat{r}_j \cdot \hat{x}) \quad (2)$$

and then calculate perturbations in the usual way, beginning with second order:

$$\Delta_2 = \sum \frac{\langle NL | v_n(x) | N'L' \rangle \langle N'L' | v_n(x) | NL \rangle}{(\epsilon_0 - \epsilon_n) + (E_{NL} - E_{N'L'})}, \quad (3)$$

where $v_n(x) = \langle 0 | H_{int} | n \rangle$. In principle, we could evaluate this sum, including excited states of both the core (n) and the outer electron (N', L'). Not only would this be somewhat difficult but it would have to be repeated for every value of N and L in which we were interested. Instead, we make the

assumption (justified after the fact) that the excitation energies of the core are larger than those of the outer electronic system. (This looks reasonable, but there are certainly some huge excitation energies of the Rydberg electron up into the continuum that we hope are “negligible”). Then we expand the denominator of Eq.(3) in a binomial series:

$$\Delta_2 \approx \sum_n \frac{\langle NL | v_n(x) | N'L' \rangle \langle N'L' | v_n(x') | NL \rangle}{\epsilon_0 - \epsilon_n} \left[1 + \frac{E_{N'L'} - E_{NL}}{\epsilon_0 - \epsilon_n} + \dots \right] \quad (4)$$

In the first term above it is easy to apply closure over the intermediate states $N'L'$ to obtain an effective “adiabatic” potential

$$V_{ad} = \sum_n \frac{v_n(x)v_n(x)}{\epsilon_0 - \epsilon_n} = - \sum_{l=1} \frac{\alpha_l}{x^{2(l+1)}} \quad (5)$$

whose expectation value $\langle NL | V_{ad}(x) | NL \rangle$ gives the leading correction to the energy. The second sum in Eq. (5) cannot be carried out to ∞ because the higher terms would diverge; the series is probably asymptotic and should be terminated at its smallest term.

The second term in Eq. (4) seems harder to convert into effective potential form because of the energy-dependent factor, but a simple trick solves this problem:

$$\sum_n \frac{\langle NL | v_n(x) | N'L' \rangle \langle N'L' | v_n(x') | NL \rangle (E_{N'L'} - E_{NL})}{(\epsilon_0 - \epsilon_n)^2} = \langle NL | \sum_n \frac{v_n(x) [H_0(x), v_n(x)]}{(\epsilon_0 - \epsilon_n)^2} | NL \rangle. \quad (6)$$

By converting the energy dependence to a commutator we are able to carry out the closure sum; I think the first time this trick was used may have been by Mittleman and Watson [5]. After commutation and integration by parts, this “first nonadiabatic term” takes the following form:

$$V_{nad}(x) = \frac{1}{2} \sum_n \frac{\nabla_x^2 v_n^2(x)}{(\epsilon_0 - \epsilon_n)^2} = \sum_l \frac{(l+1)(2l+1)\beta_l}{x^{2l+4}}, \quad (7)$$

where β_l is just like α_l , but with one more power of the energy difference in the denominator. And of course higher terms can be computed in a similar way. (This way of describing the process of constructing the effective potential is easy to understand, but I prefer a more formal method using projection operators that is described in detail in my chapter of the Casimir book [6].)

In any case, the effective potential can be written out to the term of order x^{-8} as follows:

$$U(x) = -\frac{\alpha_1}{x^4} + \frac{6\beta_1 - \alpha_2}{x^6} + \frac{\delta + 16\gamma_1/5}{x^7} + \frac{15\beta_2 - \alpha_3 - \epsilon + \alpha_1\beta_1 - 72\gamma_1 [1 + L(L+1)/10]}{x^8}. \quad (8)$$

In a series of papers [7] which are summarized in perhaps excessive detail in Ref.[6] I applied this method to the Rydberg states of helium, and I even included terms up to order x^{-10} with considerable success. Of course, in that case all the coefficients that appear in the effective potential can be evaluated exactly and analytically, since the core is simply a hydrogenic ion. In the case of lithium, the core is a two-electron system, and the sums giving the various coefficients must be performed numerically. To calculate them, we used the method of pseudostate summation; that is, we replaced the complete set of states $|n\rangle$ by a finite and discrete set of pseudostates. These are in the form of prediagonalized Hylleraas expansions, and ϵ_n is replaced by the corresponding expectation value of the Hamiltonian. This method converges well, and the effective potential is (for ${}^7\text{Li}$, with mass-dependent effects included) the following [8]:

$$U(x) = -\frac{0.19248540}{x^4} + \frac{0.097881}{x^6} + \frac{0.143125}{x^7} - \frac{0.428584 + 0.049005L(L+1)}{x^8} \quad (9)$$

It is now only necessary to evaluate the expectation values of the inverse powers of x in the appropriate hydrogenic state (N,L) to obtain our values of the energy shifts, and there are very well known formulas for that. (Actually, small second-order terms, given analytically, must also be included to the accuracy needed here.)

After this nonrelativistic calculation it is possible to add some other small corrections [9]. These include relativistic effects, which we treat with the Breit-Pauli operator, the Lamb shift, and finally, the retardation correction, which is the main topic of this meeting. Remarkably, inclusion of these three corrections makes a significant improvement in the agreement of theory with experiment in the one interval (10H-10I) for which the estimated errors are small enough. The results are given in Table I. You can see that experiment agrees well with the theory, including the small corrections, for the interval 10H-10I, while the results are not definitive for the 10G-10H interval.

III. MOLECULAR HYDROGEN ION

Inspired by recent experiments on the fine structure of Rydberg states of the hydrogen molecule by Lundeen's group [10] and their analysis in terms of an effective potential similar to that described above, we [11] have tried to calculate the dipole polarizability of the hydrogen molecular ion, H_2^+ . We had tried to use our Hylleraas variational method to calculate the ground state of this ion some years ago without quantitative success; this type of trial function is clearly designed for atomic systems rather than the more localized motion of the very massive nuclei. But we have recently been more successful by allowing very high powers of the internuclear coordinate to be included. For example, the function $R^N e^{-\alpha R}$, with $\alpha=N/2$, produces a function peaked at $R=2$, close to the adiabatic equilibrium point, and if N is large enough the function can represent the Gaussian-like vibrational wave function of the ion quite well. Using a ground-state wave function with 308 terms

and including up to 364 intermediate p-pseudostates, we find the polarizability of the ion to be $3.16795 a_0^3$, to be compared with the experimental result [10] of $3.1681(7) a_0^3$. This agreement is good, although our result is not yet completely converged. I am not sure whether it is practical to hope that in the future theory and experiment will be able to observe Casimir effects in H_2 .

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TABLE I

Comparison of level differences for ${}^7\text{Li}$, in MHz, between theory and experiment [2].

The standard deviations of the differences are experimental and theoretical combined in quadrature.

Interval	Theory	Experiment	Experiment-Theory
10G-10H	$339.697 \pm .115$	$339.7186 \pm .0031$	0.02 ± 0.11
10H-10I	$109.2137 \pm .0011$	$109.2140 \pm .0047$	0.0003 ± 0.0048

