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Polarizabilities of two-electron positive ions and Rydberg levels of lithium

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We have carried out precision calculations of various second-order sums for the two-electron positive ions Li^{+}, Be^{2+}, and B^{3+}. These have the form $\sum_N \langle 0|V|N\rangle\langle N|V|0\rangle/(E_N-E_0)^k$, where $k=1,2,3$. The perturbation V is in each case a multipole-potential term, and for $k=1$ the sum corresponds to the usual definition of multipole polarizability. The initial state 0 and the intermediate states N are constructed from two-particle Hylleraas basis sets of the appropriate symmetry and angular momentum. Although the set N does not contain any true continuum functions, the pseudostates represent the continuum very well, and excellent convergence is obtained. These two-body quantities are then used to evaluate the energy levels of three-electron systems in high Rydberg states by the asymptotic-optical-potential method previously used for two-electron systems, retaining all terms up to order x^{-6}. The results are good, but they can be still further improved by including higher-order terms, which will require multiple summation over intermediate states.

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I. INTRODUCTION TO LITHIUMLIKE RYDBERG STATES

The pseudostate summation method has proven to be very successful in the evaluation of second-order sums [1] for a variety of interesting processes, including two-photon transitions and van der Waals coefficients. Multipole polarizabilities are defined in terms of second-order sums too, and they are likely to be accurately obtainable in the same way. Recently, the usefulness of asymptotic expansions of the interaction between the Rydberg electron and the core electron in highly excited states of helium has been reemphasized [2]. For this kind of analysis it is necessary to know a variety of parameters describing the core, including its multipole polarizabilities and other quantities expressible as weighted sums over complete sets of states. In the case of heliumlike systems the core is hydrogenic, and all such sums can be obtained exactly and analytically [3]. The next more complicated system is the three-electron atom or ion with two electrons in a spherical core and one in a high Rydberg state. Here the core polarizability cannot be obtained exactly, but the analysis is otherwise the same. We are motivated by our interest in such lithiumlike states to compute some of the relevant properties of the two-electron core.

In this paper we are interested only in second-order sums over a single complete set; it is consistent with this limitation to represent the interaction between valence electron and core in terms of the following optical potential:

$$U(x)=-\frac{\alpha_1}{x^4}+\frac{6\beta_1-\alpha_2}{x^6}\ , \qquad (1)$$

where α_1 and α_2 are dipole and quadrupole polarizabilities, respectively, and β_1 is the first nonadiabatic coefficient (all to be defined below). The first-order shift in the energy of any hydrogenic valence electron with quantun numbers N and L due to this potential is

$$\Delta_1=\int d^3x\ \Psi_{NL}(\mathbf{x})U(x)\Psi_{NL}(\mathbf{x})\ . \qquad (2)$$

The main result of this paper is to calculate sets of these coefficients for the ground states of the isoelectronic series Li^{+}, Be^{2+}, and B^{3+}, and to evaluate some fine-structure intervals in the case of Li.

We begin by writing the Hamiltonian for the system consisting of three electrons of unit mass and a nucleus of mass M and charge Z. We assume that electron number 3 is the valence electron and is much further from the nucleus than the other two. Then with energy in rydbergs the Hamiltonian is

$$H=-\nabla_1^2-\nabla_2^2-\nabla_3^2-\frac{1}{M}\nabla_M^2-\frac{2Z}{|\mathbf{r}_1-\mathbf{r}_M|}-\frac{2Z}{|\mathbf{r}_2-\mathbf{r}_M|}$$
$$-\frac{2Z}{|\mathbf{r}_3-\mathbf{r}_M|}+\frac{2}{|\mathbf{r}_1-\mathbf{r}_2|}+\frac{2}{|\mathbf{r}_1-\mathbf{r}_3|}+\frac{2}{|\mathbf{r}_2-\mathbf{r}_3|}\ . \qquad (3)$$

The next step is to change to scaled, semi-Jacobi variables describing, respectively, the location of the center of mass in the laboratory frame, the positions of the two core electrons relative to the nucleus, and the position of the valence electron (3) relative to the center of mass of the two-electron core. These are

$$\begin{aligned}\mathbf{R}&=\frac{\mathbf{r}_1+\mathbf{r}_2+\mathbf{r}_3+M\mathbf{r}_M}{M+3}\ ,\\ \boldsymbol{\rho}_{1,2}&=m(\mathbf{r}_{1,2}-\mathbf{r}_M)\ ,\\ \mathbf{x}&=m'\left[\mathbf{r}_3-\frac{\mathbf{r}_1+\mathbf{r}_2+M\mathbf{r}_M}{M+2}\right]\ .\end{aligned} \qquad (4)$$

Here $m\equiv M/(M+1)$ is the reduced mass of one electron and the nucleus, while $m'\equiv(M+2)/(M+3)$ is the reduced mass of the valence electron and the core. Then we can write the unperturbed Hamiltonian of the two-electron core, in reduced Rydberg units $R=m\mathcal{R}$ ($\mathcal{R}$ is the Rydberg constant) as

$$H_{0c}=-\nabla^2_{\rho_1}-\nabla^2_{\rho_2}-K\nabla_{\rho_1}\cdot\nabla_{\rho_2}-\frac{2Z}{\rho_1}-\frac{2Z}{\rho_2}+\frac{2}{|\boldsymbol{\rho}_1-\boldsymbol{\rho}_2|}\ , \tag{5}$$

where $K=2/(M+1)$, while the Hamiltonian for the valence electron, in the same units, is

$$H_{0v}=-q\left[\nabla^2_x+\frac{2(Z-2)}{x}\right]\ , \tag{6}$$

where $q\equiv m'/m\simeq 1+K^2/2$. The three-electron unperturbed wave function, an eigenfunction of $H_{0c}+H_{0v}$, clearly has the form of the product of a heliumlike and a shielded hydrogenic wave function. The interaction potential has the form

$$V=2q\left[\frac{1}{|\mathbf{x}-f\boldsymbol{\rho}_1+g\boldsymbol{\rho}_2|}+\frac{1}{|\mathbf{x}-f\boldsymbol{\rho}_2+g\boldsymbol{\rho}_1|}-\frac{Z}{|\mathbf{x}+g(\boldsymbol{\rho}_1+\boldsymbol{\rho}_2)|}+\frac{(Z-2)}{x}\right]\ , \tag{7}$$

where

$$f=\frac{(M+1)q}{(M+2)}=\frac{1}{(1+K/2-K^2/2)}\ ,$$

$$g=\frac{q}{(M+2)}=\frac{Kf}{2}\ .$$

We are interested in the case of $x\gg\rho_i$ and make an expansion in Legendre polynomials in the usual way,

$$V\simeq\frac{2}{x^2}\left[1+\frac{K(Z-2)}{2}\right](\mathbf{w}\cdot\hat{\mathbf{x}})+\frac{2}{x^3}[\rho_1^2P_2(\hat{\boldsymbol{\rho}}_1\cdot\hat{\mathbf{x}})+\rho_2^2P_2(\hat{\boldsymbol{\rho}}_2\cdot\hat{\mathbf{x}})-Kw^2P_2(\hat{\mathbf{w}}\cdot\hat{\mathbf{x}})]+\cdots\ , \tag{8}$$

where $\mathbf{w}=\boldsymbol{\rho}_1+\boldsymbol{\rho}_2$, and where we have kept terms up to first order in K. From these two terms in $1/x$ we can construct the first two terms in the optical potential shown in Eq. (1).

II. SECOND-ORDER PERTURBATION CALCULATIONS

We now wish to use the potential V, in its multipole form [Eq. (8)], in second-order perturbation theory. From Ref. [2] the appropriate definitions are

$$\alpha_i\equiv\sum_N\frac{\langle 0|v_i|N\rangle\langle N|v_i|0\rangle}{(E_N-E_0)}\ ,$$
$$\beta_i\equiv\sum_N\frac{\langle 0|v_i|N\rangle\langle N|v_i|0\rangle}{(E_N-E_0)^2}\ . \tag{9}$$

(In addition, we will evaluate coefficients, γ_i, with cubic denominators, which may be of interest later on.) Here we let the potential in Eq. (8) be $V=v_1/x^2+v_2/x^3$ and will insert these coefficients in Eq. (1) to derive the optical potential. For the two-electron isoelectronic series the ground state 0 will have the Hylleraas form

$$\Psi_0=e^{-(a\rho_1+b\rho_2)}\sum_{i,j,k}C_{ijk}\rho_1^i\rho_2^j\rho_{12}^k+[(1,2)\rightarrow(2,1)]\ . \tag{10}$$

The pseudostate method [1] uses a set of normalizable functions to approximate the complete set represented by $|N\rangle$ in Eq. (9). In our case, these have the Hylleraas form as well, but with angular momentum 1 or 2 for the dipole or quadrupole terms of Eq. (8), respectively. That is, for $L=1$,

$$\Psi_P=-\cos(\theta_{12}/2)(f+\tilde{f})\mathcal{D}_1^{1+}-\sin(\theta_{12}/2)(f-\tilde{f})\mathcal{D}_1^{1-}\ , \tag{11}$$

where

$$f(\rho_1,\rho_2,\rho_{12})=e^{-(\gamma\rho_1+\delta\rho_2)}\rho_1\sum_{i,j,k}C_{ijk}\rho_1^i\rho_2^j\rho_{12}^k\ ,$$

$$\tilde{f}(\rho_1,\rho_2,\rho_{12})=f(\rho_2,\rho_1,\rho_{12})\ .$$

Similarly, for $L=2$ we have

$$\begin{aligned}\Psi_D={}&(f+\tilde{f})[-\mathcal{D}_2^{0+}+\sqrt{3}\cos(\theta_{12})\mathcal{D}_2^{2+}]\\&+\sqrt{3}\sin(\theta_{12})(f-\tilde{f})\mathcal{D}_2^{2-}\\&+(g+\tilde{g})[-\cos(\theta_{12})\mathcal{D}_2^{0+}+\sqrt{3}\mathcal{D}_2^{2+}]\ ,\end{aligned} \tag{12}$$

where

$$f(\rho_1,\rho_2,\rho_{12})=e^{-(\gamma\rho_1+\delta\rho_2)}\rho_2^2\sum_{i,j,k}C_{ijk}^{(1)}\rho_1^i\rho_2^j\rho_{12}^k\ ,$$

$$g(\rho_1,\rho_2,\rho_{12})=e^{-(\gamma\rho_1+\delta\rho_2)}\rho_1\rho_2\sum_{i,j,k}C_{ijk}^{(2)}\rho_1^i\rho_2^j\rho_{12}^k\ ,$$

$$\tilde{f}(\rho_1,\rho_2,\rho_{12})=f(\rho_2,\rho_1,\rho_{12})\ ,$$

$$\tilde{g}(\rho_1,\rho_2,\rho_{12})=g(\rho_2,\rho_1,\rho_{12})\ .$$

The rotational harmonics $\mathcal{D}$ appearing here were defined by Bhatia and Temkin [4]. Using these forms, we obtain variational wave functions for the initial ^1S state and the set of intermediate pseudostates for each value of Z from 3 through 5. These are then inserted in Eq. (9) along with the corresponding variational energies to obtain the quantities of interest.

III. RESULTS OF THE PERTURBATION CALCULATIONS

In Table I we show the convergence of the dipole polarizability of Li$^+$ with respect to the expansion length of the S-wave ground state and the number of P-wave intermediate pseudostates. The convergence is seen to be very rapid, and it improves with increasing Z. In Table II the results for the three sums of interest (for both dipole and quadrupole) are listed for $Z=3,4,5$. These are very similar to the previous results [5], some of which have been obtained by perturbation methods similar to the present one, while others have used variational techniques. Better results are usually obtained when correlations are explicitly included in the wave functions, although the Hartree method gives fairly good values as well. As usual, much of the present work was prefigured by Drake

TABLE I. Convergence of the dipole polarizability of the ground state of $^7\mathrm{Li}^+$ with respect to the parameters N_s (the expansion length of the ground state) and N_p (the number of intermediate pseudostates). Mass polarization is included in the Hamiltonian, and the factor $1+K$ from Eq. (8) is also present.

N_s N_p	50	70	95	125
35	0.192 483 81	0.192 483 02	0.192 482 72	0.192 482 75
56	0.192 485 91	0.192 484 91	0.192 484 83	0.192 484 71
84	0.192 486 47	0.192 485 47	0.192 485 36	0.192 485 28
120	0.192 486 64	0.192 485 61	0.192 485 51	0.192 485 42

[6], whose results for α_1 and β_1 are almost as accurate as the present ones.

IV. RYDBERG STATES OF LITHIUM

We are particularly interested here in very precise values for the splitting between levels of high L in the same N manifold; these have been measured in helium with exquisite precision [7], and similar measurements should be practical in lithium as well. As a first approximation, we have calculated the splittings for $N=10$ in $^7\mathrm{Li}$, using the results of Table II for α_1, β_1, and α_2. Since only the first two terms in the expansion of the optical potential have been computed [Eq. (1)], we use the following conservative expression for the energy shift $\Delta(NL)$ away from the unperturbed energy $-R/N^2$:

$$\Delta(NL)=R\,[(V_4+\tfrac{1}{2}V_6)\pm\tfrac{1}{2}V_6]\,, \tag{13}$$

where $R=\mathcal{R}(1-K/2)=3.289\,584\,678\times10^9$ MHz, for $^7\mathrm{Li}$, and where V_4 and V_6 are the expectation values of the two terms in Eq. (1) to be evaluated analytically using expressions like those given by Bockasten [8]. At this level of accuracy it is necessary to include a relativistic correction whose L-dependent part is [2,9]

$$\Delta_{\mathrm{rel}}=-\frac{R'}{N^3(L+\frac{1}{2})}\,,$$

$$\text{where } R'=\alpha^2R=1.751\,749\times10^5\ \text{MHz}\,. \tag{14}$$

In Table III the fine-structure splittings for this case are shown, and these might be measurable by the techniques of Ref. [7]; if so it will be necessary to improve our accuracy by adding higher terms in $1/x$ as well as additional relativistic corrections. Note that α_1 must be known to an accuracy of at least 1×10^{-4} to be consistent with the estimates of error given here.

TABLE II. Adiabatic and nonadiabatic polarizabilities for three isoelectronic systems. Mass polarization is included only in the Li^+ dipole case, but the factor $1+K(Z-2)$ is included in all the dipole results. Numbers in square brackets denote powers of 10.

System	Li^+	Be^{2+}	B^{3+}
α_1	0.192 485	0.052 282	0.019 651
β_1	0.035 29	4.919[−3]	1.125[−3]
γ_1	6.806[−3]	4.847[−4]	6.723[−5]
α_2	0.113 89	0.015 32	3.427[−3]
β_2	0.016 68	1.132[−3]	1.524[−4]
γ_2	2.584[−3]	8.819[−5]	7.136[−6]

TABLE III. Fine-structure energy shifts in the $N=10$ manifold of $^7\mathrm{Li}$. Dipole and quadrupole terms are included up to x^{-6} as described in the text, and the leading relativistic term is also included.

Interval	Energy shift (MHz)
$10G$-$10H$	340.62±1.18
$10H$-$10I$	109.361±0.153
$10I$-$10K$	42.816±0.028
$10K$-$10L$	19.480±0.006
$10L$-$10M$	10.0097±0.0015

A recent calculation [10] of the lower-lying Rydberg states of lithium is in the same spirit as the present work. A polarized-orbital ansatz is used there to represent the distortion of the atomic core by the valence electron, but the asymptotic expansion is not made. For this reason it is possible to treat S, P, and D states numerically. Nevertheless, the values of the polarizabilities and the nonadiabatic coefficients are calculated only in the Hartree-Fock approximation for the two-electron core and are not as good as the present ones. Agreement with experiment is obtained but not to the accuracy we need for the higher states. The Casimir effect for a multielectron core system and a Rydberg electron has been discussed recently [11], and estimates have been made for the three-electron systems of interest here.

V. CONCLUSIONS

We have presented the results of a systematic calculation of polarization-type sum rules for two-electron isoelectronic systems, obtained by representing the intermediate states by discrete pseudostates. Convergence is generally good and improves (as expected) with increasing nuclear charge as correlation decreases in importance. The results for Li^+ are used to calculate splittings in high Rydberg states of $^7\mathrm{Li}$; even with the limited expansion (up to x^{-6}) used here to represent the nonrelativistic optical potential, the accuracy for the $10L$-$10M$ transition is about 1.5 kHz. We hope that this work will encourage experimental measurement of these splittings and a further analysis of the theory of relativistic and retardation effects.

We are now in the final stages of a series of similar calculations for the polarizabilities of the helium atom, which converge rather more slowly. Still more difficult is the negative hydrogen ion (H^-); it is of interest in the study of excited states of the "molecule" PsH [12]. Finally, we are also computing the polarizabilities of the positronium ion (Ps^-). These last two require many more terms in the expansions, and will also benefit from extrapolation techniques [13].

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