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Polarizabilities and susceptibilities from high-angular-momentum Rydberg states of halogen and inert-gas isoelectronic sequences

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We have developed perturbative expressions for the energies of high-angular-momentum Rydberg states of halogen and inert-gas isoelectronic sequences. These expressions allow us to determine polarizabilities and estimate susceptibilities of the cores. They also provide simple expressions for the quantum defects.

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I. INTRODUCTION

Rydberg states have attracted considerable attention because of their resemblance to hydrogenic states. However, there are some differences between the two. These differences are related to the interaction of the Rydberg electron, i.e., the electron in the highly excited state, with the core. An analysis of these differences can yield important information about the properties of the core.

A. A brief review

The subject of Rydberg atoms has been reviewed many times [1–4]. The energy levels of these atoms or ions are conveniently described by the Rydberg formula

$$W=-\frac{RZ_c^2}{(n-\delta)^2},\quad n\gg 1\ , \tag{1.1}$$

where R is the Rydberg constant, Z_c is the charge of the core in units of e, and δ is the quantum defect which is expected to be independent of n for $n \gg l$. The case of Rydberg states of alkali-metal atoms has attracted special attention. Here the quantum defect in the leading approximation for $n \gg l \gg 1$ is related [5] to the polarizabilities of the core. It has been found [6] that even the small quadrupolar polarizability term is needed to provide a satisfactory explanation of the accurate experimental observations [7] of the energy levels for $l = 3,4,5$.

For the halogen and inert-gas isoelectronic sequences, the situation is considerably more complicated. In this case, the analysis for large-l Rydberg states is carried out within the framework of pair coupling [8] where the levels are formed in groups of close-lying pairs. The l of the Rydberg electron couples with the J of the parent giving rise to a K which then couples with the spin of the Rydberg electron giving J_{final}:

$$(J,l)\to K\ , \tag{1.2}$$

$$(K,\tfrac{1}{2})\to J_{\text{final}}\ . \tag{1.3}$$

The energy levels of the Rydberg states of halogen and inert-gas isoelectronic sequences with large l are given by

$$E(J,K,l,n)=b(J,l,n)+f(J,K,l)d(l,n)\quad \text{for } n\gg l\gg 1\ . \tag{1.4}$$

The expressions for $f(J,K,l)$ are as follows [9,10].

1. Halogen isoelectronic sequences

$$\begin{aligned}
f(2,l+2,l)&=\frac{1}{10}\left[\frac{2l}{2l+3}\right],\\
f(2,l+1,l)&=-\frac{1}{20}\left[\frac{2l+12}{2l+3}\right],\\
f(2,l,l)&=-\frac{1}{10}\frac{(2l-3)(2l+5)}{(2l-1)(2l+3)},\\
f(2,l-1,l)&=-\frac{1}{20}\left[\frac{2l-10}{2l-1}\right],\\
f(2,l-2,l)&=\frac{1}{10}\left[\frac{2l+2}{2l-1}\right],\\
f(1,l+1,l)&=-\frac{1}{20}\left[\frac{2l}{2l+3}\right],\\
f(1,l,l)&=\frac{1}{10},\\
f(1,l-1,l)&=-\frac{1}{20}\left[\frac{2l+2}{2l-1}\right],\\
f(0,l,l)&=0\ .
\end{aligned} \tag{1.5}$$

2. Inert-gas isoelectronic sequences

$$f(J,K,l)=-\frac{6h^2+3h-2J(J+1)l(l+1)}{8J(J+1)(2l-1)(2l+3)}\ , \tag{1.6}$$

with

$$2h=K(K+1)-J(J+1)-l(l+1)\ .$$

Exchange interactions and mixing with other states then give rise to finer corrections including the splitting of each pair with a given K.

B. An outline of our work

The main purpose of our work is to analyze the large-angular-momentum Rydberg levels of halogen and inert-gas isoelectronic sequences within a perturbative approach. The unperturbed states are taken to be the pair-coupling states with the Rydberg-electron spin not taken into account. The successive perturbation corrections to the energy levels are related to the properties of the core, such as the dipolar polarizability and the diamagnetic susceptibility. Comparison of the energies with the observed energies allows us to predict the polarizabilities and susceptibilities of the parent core. These predictions are found to be in good agreement with the results of Hartree-Fock calculations [11]. Reversing the argument, if we have good estimations for the input values of the polarizabilities and susceptibilities, we can predict fairly accurately the energy levels of all Rydberg states with large l, for all halogen and inert-gas isoelectronic sequences, in terms of a single parameter.

II. PERTURBED RYDBERG ENERGIES

Here we develop perturbative expressions for the energies of high-angular-momentum Rydberg states, and discuss their limitations.

A. General perturbative approach

Consider an atom or ion with N electrons and atomic number Z. Ignoring exchange contributions, one has for the perturbed energy of the Rydberg state (we use atomic units $e=\hbar=m_e=1$)

$$\delta E = V_{00} + \sum_{t(\neq 0)} \frac{|V_{0t}|^2}{E_0 - E_t} + \cdots \ , \tag{2.1}$$

$$V_{ts} = \langle \psi_t | V | \psi_s | \rangle \ , \tag{2.2}$$

where V is the perturbing interaction

$$V(\mathbf{R},\mathbf{r}_i) = \sum_i \left[\frac{1}{|\mathbf{R}-\mathbf{r}_i|} - \frac{1}{R} \right] , \tag{2.3}$$

$\mathbf{R}$ is the position of the Rydberg electron. Contribution of the degenerate or nearly degenerate states is discussed later. In the following discussion we confine ourselves to the problem of Rydberg states in halogen and inert-gas isoelectronic sequences. For these, the pair-coupling scheme is appropriate, which means that our states will be characterized as follows.

1. *Halogen isoelectronic sequences*

$$\begin{aligned} &K = l+1, l, l-1, l+2, l-2 \quad (P_2) \ , \\ &K = l-1, l+1, l \quad (P_1) \ , \\ &K = l \quad (P_0) \ , \end{aligned} \tag{2.4}$$

where $P_{2,1,0}$ are the parent states of the halogen isoelectronic sequences.

2. *Inert-gas isoelectronic sequences*

$$\begin{aligned} &K = l-\tfrac{3}{2}, l+\tfrac{3}{2}, l-\tfrac{1}{2}, l+\tfrac{1}{2} \quad (P_{3/2}) \ , \\ &K = l+\tfrac{1}{2}, l-\tfrac{1}{2} \quad (P_{1/2}) \ , \end{aligned} \tag{2.5}$$

where $P_{3/2,1/2}$ are the parent states of the inert-gas isoelectronic sequences. We will be neglecting the small splitting of these states due to the spin of the Rydberg electron.

For Rydberg states, the region of importance is $R \gg 1$, so that the following expansion is useful in the evaluation of the matrix elements:

$$\begin{aligned} V(R,r_i) = \sum_i & \left[\left[\frac{1}{r_i} - \frac{1}{R} \right] \Theta(r_i - R) \right. \\ & \left. + \sum_{l=1}^{\infty} \frac{r_<^l}{r_>^{l+1}} P_l(\cos\theta_i) \right] , \end{aligned} \tag{2.6}$$

$$\cos\theta_i = \hat{\mathbf{R}} \cdot \hat{\mathbf{r}}_i \ ,$$

where $r_<$ ($r_>$) is the smaller (larger) of (R, r_i). The first term gives rise to what is known as the penetration term which is generally quite small for high-angular-momentum Rydberg states [6] and will be neglected.

B. First-order contribution

In evaluating the first-order contribution to δE, we note that only the $l=2$ term in Eq. (2.6) contributes to the states with $P_{2,1,0}$ parents for halogen isoelectronic sequences and $P_{3/2,1/2}$ parents for inert-gas isoelectronic sequences. The general form of the first-order contribution neglecting penetration or $R < r_i$ region, is

$$\begin{aligned} \delta E^{(1)} &= V_{00} \\ &= g_c f(J,K,l) \int R^{-3} |R_{n,l}(R)|^2 R^2 dR \ , \end{aligned} \tag{2.7}$$

where g_c depends only on the spatial properties of the core, $f(J,K,l)$ is given in Eqs. (1.5) and (1.6), and $R_{n,l}$ are the Coulombic radial wave functions. Carrying out the integrations we get

$$\delta E^{(1)} = g_c f(J,K,l) \frac{8 Z_c^3 (2l-1)!}{n^3 (2l+2)!} \ , \tag{2.8}$$

where Z_c is the charge of the core, $Z_c = Z - N + 1$. To obtain any further information about g_c we need detailed knowledge about the structure of the wave function. For this we consider the asymptotic wave function of the core.

It follows from the quantum numbers of the various halogen ions that the core wave function for halogen isoelectronic sequences is of the form [13]

$$\phi_0^{(N-1)} \rightarrow \hat{\mathbf{r}}_1 \eta_1(r_1) \phi_0^{(N-2)}(r_i) \ , r_1 \gg r_i, \quad i \neq 1 \ , \tag{2.9}$$

where $\eta_1(r_1)$ does not depend on angles, and $\phi_0^{(N-2)}$ is the ground-state wave function of the $(N-2)$ electron system with vanishing total orbital angular momentum. Then the contribution of this domain to the energy is

$$\delta E^{(1)} \approx f(J,K,l)\int r_1^2|\phi_0^{(N-1)}|^2 r_1^2 dr_1 \times \prod_{i\,(\neq 1)} d^3r_i \int \frac{1}{R_3}|R_{n,l}(R)|^2 R^2 dR\;, \qquad r_1 \gg r_i,\quad i\neq 1\;. \tag{2.10}$$

The expectation value of r_1^2 in Eq. (2.10) represents the contribution of the outer electron in the $(N-1)$-electron system to 6χ, where χ is the diamagnetic susceptibility of the system. However, in this integral, the contribution is only from the large-r_1 region. Since this contribution is an important part of the expectation value of r_1^2, we expect it to be proportional to but somewhat smaller than $6(\chi_{N-1}-\chi_{N-2})$ where χ_i is the diamagnetic susceptibility of the i-electron system. Therefore we may replace it by $A(\chi_{N-1}-\chi_{N-2})$ where A is expected to be somewhat less than 6. This leads to

$$\delta E^{(1)} = A(\chi_{N-1}-\chi_{N-2}) f(J,K,l)\frac{8Z_c^3(2l-1)!}{n^3(2l+2)!}\;. \tag{2.11}$$

For the inert-gas isoelectronic sequences, the core wave function has the form

$$\phi_0^{(N-1)} \to \hat{\mathbf{r}}_1\times\hat{\mathbf{r}}_2\eta_1(r_1)\eta_2(r_2)\phi_0^{(N-3)}(r_i) \qquad r_1 \gg r_2 \gg r_i,\quad i\neq 1,2, \tag{2.12}$$

where $\eta_1(r_1)$ and $\eta_2(r_2)$ do not depend on angles, and $\phi_0^{(N-3)}$ is the ground-state wave function of the $(N-3)$-electron system with vanishing total orbital angular momentum. Then the contribution of this domain to the energy is

$$\delta E^{(1)} \approx f(J,K,l)\int (r_1^2+r_2^2)|\phi_0^{(N-1)}|^2 r_1^2 dr_1 r_2^2 dr_2 \times \prod_{i\,(\neq 1,2)} d^3r_i \int \frac{1}{R^3}|R_{n,l}(R)|^2 R^2 dR\;, \qquad r_1 \gg r_2 \gg r_i,\quad i\neq 1,2\;. \tag{2.13}$$

Following the same arguments as for halogens, we get

$$\delta E^{(1)} = A(\chi_{N-1}-\chi_{n-3}) f(J,K,l)\frac{8Z_c^3(2l-1)!}{n^3(2l+2)!}\;. \tag{2.14}$$

Comparison of Eqs. (2.11) and (2.14) with Eq. (2.8) implies that effectively we have taken g_c to be

$$g_c = \begin{cases} A(\chi_{N-1}-\chi_{N-2}) & \text{for halogen sequences} \\ A(\chi_{N-1}-\chi_{N-3}) & \text{for inert-gas sequences}\;. \end{cases} \tag{2.15}$$

The usefulness of this relation is that since $\frac{1}{6}A$ represents the fraction of the contribution of the asymptotic domain to the susceptibility of the outer electrons, we expect A to have approximately the same value for all the systems. Therefore we can use the values of g_c to deduce the relative values of $(\chi_{N-1}-\chi_{N-2})$ for different halogen cores and $(\chi_{N-1}-\chi_{N-3})$ for different inert-gas cores and their isoelectronic sequences.

C. Second-order contribution

The leading term in the second-order contribution to the energy is

$$\delta E^{(2)} = \sum_{t\,(\neq 0)} \frac{\left|\left\langle \psi_0 \left| \sum_i (\mathbf{r}_i\cdot\mathbf{R})/R^3 \right| \psi_t \right\rangle\right|^2}{E_0-E_t}\;. \tag{2.16}$$

In the adiabatic approximation, i.e., neglecting the Rydberg-electron energy in the denominator, one can write

$$\delta E^{(2)} = \frac{1}{3}\sum_{t\,(\neq 0)} \frac{\left|\langle \phi_0^{(N-1)}|\sum_i \mathbf{r}_i|\phi_t^{(N-1)}\rangle\right|^2}{E_0-E_t}\int \frac{1}{R^4}|R_{n,l}(r)|^2 R^2 dR - \sum_{t\,(\neq 0)}\frac{1}{E_0-E_t}\left[\frac{1}{3}\left|\left\langle \psi_0 \left| \frac{1}{R^2}\sum_i \mathbf{r}_i \right| \psi_t\right\rangle\right|^2 - \left|\left\langle \psi_0 \left| \sum_i (\mathbf{r}_i\cdot\mathbf{R})/R^3 \right| \psi_t\right\rangle\right|^2\right]\;. \tag{2.17}$$

We now obtain an estimation for the second term in Eq. (2.17), $\delta E^{(2)'}$, and argue that it is small. For this we replace E_t in the denominator by an average value $\bar{E}_t$ to get

$$\delta E^{(2)'} = \frac{1}{E_0-\bar{E}_t}\left\langle \psi_0 \left| \left[\sum_i \mathbf{r}_i\cdot\mathbf{R}/R^3\right]^2 - \frac{1}{3}\left[\sum_i \mathbf{r}_i\right]^2 \Big/ R^4 \right| \psi_0 \right\rangle\;. \tag{2.18}$$

For simplifying this expression we again use the asymptotic structure in Eqs. (2.9) and (2.12), which leads to

$$\delta E^{(2)'} \approx \frac{1}{(E_0-\bar{E}_t)}\left\langle \psi_0 \left| \sum_i \frac{2}{3}\left[\frac{r_i^2}{R^4}\right] P_2(\hat{\mathbf{r}}_i\cdot\hat{\mathbf{R}}) \right| \psi_0 \right\rangle \tag{2.19}$$

so that

$$\frac{\delta E^{(2)'}}{\delta E^{(1)}} \approx \frac{4Z_c(3n^2-l^2-l)}{3(E_0-\bar{E}_t)n^2(2l+3)(2l-1)}\;, \tag{2.20}$$

which is quite small for $l \geq 3$. Therefore, identifying the coefficient of the first term in Eq. (2.17) with the polarizability α_{N-1} of the core, we get

$$\delta E^{(2)} \approx -\tfrac{1}{2}\alpha_{N-1}\frac{16Z_c^4(3n^2-l^2-l)(2l-2)!}{n^5(2l+3)!} \ . \quad (2.21)$$

D. Off-diagonal terms

There are two classes of off-diagonal terms. In one class, they arise from the matrix elements between Rydberg states with the same n but different l. These terms involve overlap integrals of the type

$$V_{l,l+2} \sim \int R^{-3}R_{n,l}(R)R_{n,l+2}(R)R^2dR \ , \quad (2.22)$$

which turn out to be zero.

Another class of off-diagonal terms arises from the mixing between different states of the parent core. These states have slightly different energies. The energy shifts due to these terms, correct to the third order, are

$$\delta\tilde{E}(J,K,l,n) = \sum_{J'\,(\neq J)} \frac{(g_{J,J'})^2}{\Delta_{J,J'}+\delta E^{(1)}(J)-\delta E^{(1)}(J')} \ , \quad (2.23)$$

where $\Delta_{J,J'}$ is the difference in the energies of the parents J,J',

$$\Delta_{J,J'} = E_J(n\to\infty) - E_{J'}(n\to\infty) \ , \quad (2.24)$$

$\delta E^{(1)}(J)$ is the first-order energy shift for a given J,K,l,n as in Eqs. (2.11) and (2.14), and

$$g_{J,J'} = A(\Delta\chi)\frac{8Z_c^3(2l-1)!}{n^3(2l+2)!}f_{J,J'} \ , \quad (2.25)$$

with $\Delta\chi = \chi_{N-1} - \chi_{N-2}$ for halogen and $\Delta\chi = \chi_{N-1} - \chi_{N-3}$ for inert-gas isoelectronic sequences. The nonzero, off-diagonal elements of the symmetric $f_{J,J'}$ are, for halogen isoelectronic sequences [9],

$$\begin{aligned} f_{2,1} = {} & \frac{3}{10}\left[\frac{l(l+2)}{(2l+3)(2l+3)}\right]^{1/2}\delta_{K,l+1} \\ & -\frac{3}{10}\left[\frac{(l-1)(l+1)}{(2l-1)(2l-1)}\right]^{1/2}\delta_{K,l-1} \\ & -\frac{3}{10}\left[\frac{3}{(2l-1)(2l+3)}\right]^{1/2}\delta_{K,l} \ , \\ f_{2,0} = {} & \frac{1}{5}\left[\frac{2l(l+1)}{(2l-1)(2l+3)}\right]^{1/2}\delta_{K,l} \ , \end{aligned} \quad (2.26)$$

and for inert-gas isoelectronic sequences,

$$\begin{aligned} f_{3/2,1/2} = {} & -\frac{1}{20}\left[\frac{2(2l)}{(2l+3)}\right]^{1/2}\delta_{K,l+1/2} \\ & +\frac{1}{20}\left[\frac{2(2l-1)(2l+2)}{(2l+1)(2l+1)}\right]^{1/2}\delta_{K,l-1/2} \ . \end{aligned} \quad (2.27)$$

The correction due to $\delta\tilde{E}$ in Eq. (2.23) is quite small for cores with $Z_c = 1$, but becomes significant for $Z_c > 1$.

E. Total perturbed energy

Collecting the various terms, we obtain for the perturbed energy

$$\begin{aligned} \delta E = {} & A(\Delta\chi)f(J,K,l)\frac{8Z_c^3(2l-1)!}{n^3(2l+2)!} \\ & -\tfrac{1}{2}\alpha_{N-1}\frac{16Z_c^4(3n^2-l^2-l)(2l-2)!}{n^5(2l+3)!} \\ & +\delta\tilde{E}(J,K,l,n) \ , \end{aligned} \quad (2.28)$$

where $\Delta\chi$ is $(\chi_{N-1} - \chi_{N-2})$ for halogen isoelectronic sequences and $(\chi_{N-1} - \chi_{N-3})$ for inert-gas isoelectronic sequences, χ_i being the diamagnetic susceptibility of the i-electron system, $f(J,K,l)$ is given in Eqs. (1.5) and (1.6), α_{N-1} is the dipolar polarizability of the core, and the contribution $\delta\tilde{E}(J,K,l,n)$ from the off-diagonal terms is given in Eq. (2.23). Before we use this expression, it is worth considering the various terms left out. As mentioned earlier, we have neglected all the exchange and penetration terms. These terms are expected to be quite small for $l \geq 3$. For example, in the analysis [6,12] of alkali-metal-atom Rydberg states, they contribute only a few percent of the polarizability terms. While we have included the effect of off-diagonal terms coming from different parents, we have neglected higher multipolar and higher-order perturbation terms. These terms are expected to be small [6].

III. RESULTS

We can use the expression for the energy δE given in Eq. (2.28) and the experimental values of δE to determine $A\Delta\chi$ and α_{N-1}. A pair of energy shifts for any two states will allow us to determine these two quantities. Consistency of the results from different pairs will justify the correctness of Eq. (2.28).

A. Simplified equations and input data

For halogen isoelectronic sequences, the pair-coupling states are

$$\begin{aligned} & K = l+1, l, l-1, l+2, l-2 \quad (J=2) \ , \\ & K = l-1, l+1, l \quad (J=1) \ , \\ & K = l \quad (J=0) \ . \end{aligned} \quad (3.1)$$

We will designate the states by the index $i = 1, \ldots, 5$ for $J=2$, $i = 6,7,8$ for $J=1$, and $i=9$ for $J=0$, and the corresponding perturbed energies by δE_i. There will be mixing between $i=1$ and 7 states, $i=2$, 8, and 9 states, and $i=3$ and 6 states. However, the mixing leaves the sum of the eigenenergies unchanged. Therefore to simplify the calculations we consider Eq. (2.28) for $\delta E_1+\delta E_7$, $\delta E_2+\delta E_8+\delta E_9$, $\delta E_3+\delta E_6$, δE_4, δE_5, for which $\delta\tilde{E}=0$, and we need to consider only the first two terms in Eq. (2.28) with suitable sums over appropriate states.

For inert-gas isoelectronic sequences, the pair-coupling states are

TABLE I. Input data for the energies $-\delta E_i$ in cm^{-1} for $K=l+1,l,l-1,l+2,l-2$ states with P_2 as the parent, of Cl I, Br I, I I, Ne II, Na III, Ar II, and Kr II.

	l,n	$K=l+1$	l	$l-1$	$l+2$	$l-2$
Cl I	3,4	65.5	58.3	28.7	19.9	−6.7
	5	35.7	31.7	16.3	12.9	−0.9
	6	21.3	18.6	9.8	8.4	0.4
	7	13.3	12.6		5.6	
	4,5	10.6	10.2	3.9	0.3	−4.1
Br I	3,4	86.5	75.4	58.5	34.1	0.9
	5	49.2	44.1	26.0	21.5	4.1
	6	28.6		14.8	13.9	3.7
	7	18.9	16.9	10.3	9.2	2.8
	4,5	13.7	13.2	5.6	1.8	−3.7
I I	3,4	129.7	126.1	78.4	74.1	31.0
	5	74.4	59.6	68.1	46.4	24.0
	6	46.2	40.6	29.0	29.6	20.3
Ne II	4,5	20.4	19.5	6.3	−2.4	−12.0
	6	12.2	11.6	4.0	−0.9	−6.5
	7	7.8	7.5	2.7	−0.4	−3.9
Na III	3,4	326.9	293.1	159.4	55.9	−69.3
Ar II	4,5	58.6	75.8	40.5	16.9	−10.4
	6	47.7	46.0	24.6	12.7	−3.3
	7	30.9	29.7	16.5	9.1	−1.1
Kr II	3,4	941.2	821.3	619.3	559.7	368.5
	5	565.9	485.1	377.2	367.6	249.4
	6	321.3			237.0	160.5

$$K=l-\tfrac{3}{2},l+\tfrac{3}{2},l-\tfrac{1}{2},l+\tfrac{1}{2}\quad(J=\tfrac{3}{2})\,,$$
$$K=l+\tfrac{1}{2},l-\tfrac{1}{2}\quad(J=\tfrac{1}{2})\,. \tag{3.2}$$

We will designate the states by the index $i=1,\ldots,4$ for $J=\frac{3}{2}$, $i=5,6$ for $J=\frac{1}{2}$. There will be mixing between $i=3$ and 6 states, and $i=4$ and 5 states. Since the sums of eigenenergies are unchanged by the mixing, we consider Eq. (2.28) for δE_1, δE_2, $\delta E_3+\delta E_6$, and $\delta E_4+\delta E_5$ for which $\delta\tilde{E}=0$.

Experimentally, the energies are generally given with respect to the ground-state energy. Hence we have

TABLE II. Input data for the energies $-\delta E_i$ in cm^{-1}, for $J(K)=1(l-1),1(l+1),1(l),0(l)$ states with P_J, $J=1,0$ as the parents, of Cl I, Br I, I I, Ne II, Na III, Ar II, and Kr II.

	l,n	$J(K)=1(l-1)$	$1(l+1)$	$1(l)$	$0(l)$
Cl I	3,4	55.3	45.0	9.5	35.9
	5	32.0	26.3	7.6	21.8
	6	20.3	16.6	5.5	13.0
	7	12.5	10.5		
	4,5	9.4	7.1	−1.5	4.7
Br I	3,4	80.0	65.7	18.5	
	5	43.8	37.1	13.9	32.6
	4,5	14.7	12.2	2.2	9.4
I I	4,5	16.3	13.7	3.8	11.1
Ne II	4,5	16.5	12.0	−6.2	7.0
	6	10.3		−3.1	4.6
	7	6.7	5.1	−1.8	3.1
Na III	3,4	213.7	172.1	3.0	128.3
Ar II	4,5	65.7	54.8	5.3	41.4
	6	41.8	35.1	6.1	27.6
	7	27.8	23.4	5.2	18.6
Kr II	3,4	847.7	761.9	447.9	673.9
	5	510.5	491.6	325.3	497.2
	6		302.2		

TABLE III. Input data for the energies $-\delta E_i$, for (J,K) Rydberg states of Ne I, Ar I, Kr I, and Xe I.

	l,n	$(\frac{3}{2},l-\frac{3}{2})$	$(\frac{3}{2},l+\frac{3}{2})$	$(\frac{3}{2},l-\frac{1}{2})$	$(\frac{3}{2},l+\frac{1}{2})$	$(\frac{1}{2},l+\frac{1}{2})$	$(\frac{1}{2},l-\frac{1}{2})$
Ne I	3,4	18.71	11.06	2.29	−5.63	5.27	5.03
	5	9.89	6.01	1.43	−2.65	3.07	3.00
	6	5.82	3.63	0.92	−1.38	2.23	2.01
	7	3.66	2.28	0.17	−1.08	1.14	1.10
	8	2.45	1.58		−0.56	0.86	0.86
	9		1.16	0.21	−0.29		
	4,5	3.43	2.08	−0.41	−1.89	0.62	0.62
Ar I	3,4	63.09	44.37	21.62	1.61	29.84	28.70
	5	34.35	24.92	12.57	2.74	16.84	14.84
	6	20.61	15.17	10.29	3.55	10.72	10.12
	7	13.27	9.89	5.47	1.85	7.25	7.10
	8	9.06	7.10	4.32	1.68		
	9	7.49	4.90	2.64	1.09		
	4,5	11.19	7.75	1.08	−2.50	3.90	3.68
Kr I	3,4	90.85	67.07	34.63	8.34	47.22	44.64
	5	49.03	37.94	21.42	7.97	29.2	29.2
	6	29.72	23.1	13.7	5.85	17.5	17.5
	7	19.2	15.0	9.3	4.2		
	8	13.2	10.3	6.6			
	9	9.1	7.2	3.8			
Xe I	3,4	130.8	114.3	66.8	31.3	84.0	84.0
	5	79.9	66.6	41.7	23.6	52.0	52.0
	6	49.6	41.2	26.6	16.2	33.0	33.0
	7	32.5	27.0	17.8	11.2	22.0	22.0
	8	22.5	18.6	12.4	8.0		
	9	16.2	13.4	9.1	6.0		

$$\delta E_i = \left[E_i(n,l) - E_i(\infty) + \frac{Z_c^2}{2n^2(1+m_e/m_N)} \right] , \tag{3.3}$$

where $E_i(\infty)$ takes different values for different J states, and m_N is the mass of the nucleus. One also observes that the experimental energies are given in cm^{-1} and should be multiplied by $4.556\,335\times 10^{-6}$ to convert them into atomic units.

The data for Rydberg energy levels are scattered and are of varying accuracy. Therefore for the sake of definiteness and ready reference, we have presented in Tables I–IV what we believe to be the most accurate data for δE_i for different isoelectronic sequences, which we have used in our calculations. The data for Cl I are from Ref. [14], for Br I from Refs. [15,16], for I I from Refs. [16,17], for Ne II from Ref. [18], for Na III from Ref. [19], for Ar II from Refs. [14,20,21], and for Kr II from Ref. [22]. For inert-gas isoelectronic sequences, the data for

TABLE IV. Input data for the energies $-\delta E_i$ for (J,K) Rydberg states of charged isoelectronic sequences of inert-gas atoms.

	l,n	$(\frac{3}{2},l-\frac{3}{2})$	$(\frac{3}{2},l+\frac{3}{2})$	$(\frac{3}{2},l-\frac{1}{2})$	$(\frac{3}{2},l+\frac{1}{2})$	$(\frac{1}{2},l+\frac{1}{2})$	$(\frac{1}{2},l-\frac{1}{2})$
Ca III	4,5	234.9	179.8	76.1	16.5	116.3	111.8
	6	145.8	113.4	51.6	18.4	77.8	76.3
	7	94.1	75.0	34.8	14.7	48.0	52.2
Sc IV	4,5	498.5	390.1	194.6	75.3	266.2	255.9
	6	318.5	252.6	136.0	68.2	184.6	183.0
	5,6	117.6	91.1	18.8	−10.3	52.3	51.0
	7		59.4	13.4	−3.23	37.3	37.3
	6,7	36.8	29.0	−0.53	−10.4	14.4	14.4
Rb II	4,5	121.2	93.8	36.2	6.3	68.3	67.1
	6	73.8	59.1	26.4	8.9	46.6	45.4
	7	49.0	39.1	17.5	7.0		
	8		27.1	13.1			
Sr III	4,5	391.0	314.3	152.6	68.3	231.7	225.7
	6	244.5	201.9	101.7	56.5	154.2	150.0
	7		134.5		46.1		
	5,6	89.4	69.9	14.1	−7.1	44.4	43.0

TABLE V. The average values of α_{N-1} for different (l,n) states, obtained from solutions to Eq. (2.28), for appropriate combinations of δE_i as described in Sec. III A, their average value $\bar{\alpha}_{N-1}$ along with the predictions of HF calculations from Ref. [11]. The value given for $\bar{\alpha}_{N-1}$ of Kr II is the value corrected as discussed in Sec. III C.

l,n	Cl I	Br I	I I	Ne II	Na III	Ar II	Kr II
3,4	9.09	13.3	25.7		0.47		10.5
5	9.26	13.6	26.7				11.7
6	9.31	14.8	25.3				12.1
7	9.38	14.8					
4,5	8.71	14.6		0.841		4.82	
6				0.845		4.82	
7				0.848		4.84	
$\bar{\alpha}_{N-1}$	9.15	14.2	25.9	0.845	0.47	4.83	9.6
$\alpha_{N-1}^{\mathrm{HF}}$	9.7	14.4	25.4	0.81	0.41	5.1	8.3

TABLE VI. The average values of $A\Delta\chi$ for different (l,n) states, obtained from solutions to Eq. (2.28) for appropriate combinations of δE_i as described in Sec. III A, their average value $\overline{A\Delta\chi}$, average value of $\Delta\chi$ taking $A=3.9$ along with the predictions of HF calculations from Ref. [11], where $\Delta\chi=\chi_{N-1}-\chi_{N-2}$. We have used HF value of $\chi_{N-1}-\chi_{N-2}$ for Ne II to obtain $A=3.9$.

l,n	Cl I	Br I	I I	Ne II	Na III	Ar II	Kr II
3,4	3.29	4.55	5.66		0.65		3.36
5	3.30	4.03	5.74				3.41
6	3.37	4.51	4.12				3.53
7	3.10	4.50					
4,5	3.22	4.03		0.875		2.38	
6				0.877		2.37	
7				0.881		2.37	
$\overline{A\Delta\chi}$	3.26	4.32	5.17	0.878	0.65	2.37	3.43
$\overline{\Delta\chi}$	0.84	1.11	1.33	(0.225)	0.167	0.61	0.88
$(\Delta\chi)^{\mathrm{HF}}$	0.87	1.09	1.49	0.221	0.153	0.60	0.80

TABLE VII. The average values of α_{N-1} obtained from solutions to Eq. (2.28) for (l,n) states, their average value $\bar{\alpha}_{N-1}$ along with the predictions of HF calculations from Ref. [11].

l,n	Ne I	Ar I	Kr I	Xe I	Ca III	Sc IV	Rb II	Sr II
3,4	1.323	7.30	11.43	21.1				
5	1.327	7.13	12.12	22.2				
6	1.387	7.88	12.15	22.8				
7	1.448	7.69	12.26	23.3				
8	1.385	8.39	12.61	23.2				
9	1.216	7.73	11.58	23.7				
4,5	1.184	7.06			2.63	1.91	7.15	5.00
6					2.69	2.02	7.42	5.12
7					2.71		7.08	5.28
8							7.24	
5,6						1.79		4.47
7						1.75		
6,7						1.80		
$\bar{\alpha}_{N-1}$	1.28	7.60	12.0	22.7	2.68	1.85	7.2	5.0
$\alpha_{N-1}^{\mathrm{HF}}$	1.35	7.9	12.8	23.2	2.57	1.69	7.6	4.9

Ne I are from Refs. [14,23], for Ar I from Ref. [14], for Kr I from [24,25], for Xe I from Refs. [24,26], for Ca III from Refs. [14,27], for Sc IV from Ref. [14], for Rb II from Ref. [28], and for Sr III from Ref. [29].

B. Polarizabilities and susceptibilities

In Tables V–VIII, we have given the average values of α_{N-1} and $A(\Delta\chi)$ for different (n,l) states of halogen and inert-gas isoelectronic sequences. The average of these values is recommended as being correct to within 10%. These values are given in Tables V–VIII along with the predictions of Hartree-Fock (HF) calculations [11]. We have also given the values of $\Delta\chi$ with

$$A=3.9 \tag{3.4}$$

chosen so as to give HF value of $\chi_{N-1}-\chi_{N-2}$ for Ne II. The agreement between the two is generally good. However, it may be noted that the HF values themselves may be subject to serious errors.

For positively charged ions which are isoelectronic sequences of halogen and inert-gas atoms, the radii of the Rydberg electron get reduced more than the reduction in the size of the core. As a result we prefer to use larger values of l for the penetration and other effects to be negligible.

C. Discussion

We have obtained an expression for the energies of high-angular-momentum Rydberg states of halogen and inert-gas isoelectronic sequences in terms of dipolar polarizability α_{N-1} of the core, and difference $\Delta\chi$ between the susceptibility of the core and the susceptibility of the core from which one (for halogens) or two (for inert gases) electrons are removed. We have also included the correction due to mixing of some parent states, leading to the final expression in Eq. (2.28). Using experimental values of energies and $A=3.9$ chosen so as to give the HF value of $\Delta\chi$ for Ne II, we have obtained the polarizabilities α_{N-1} and $\Delta\chi$. These predictions are in good agreement with the results of HF calculations [11]. It may be emphasized that the predictions for the polarizabilities α_{N-1} are independent of the assumption that A is approximately the same for all systems.

There is an important source of error in the experimental input. It may be noted that even a small error in $E_i(\infty)$ can lead to significant errors in the results. If Δ cm^{-1} is the error in $E_i(\infty)$, i.e., $E_i(\infty)=E_i^{\rm exact}(\infty)+\Delta$, α_{N-1} predicted is

$$\alpha_{N-1}^{\rm pred}=\alpha_{N-1}^{\rm exact}+\Delta\frac{n^5(2l+3)!(4.556\times10^{-6})}{8Z_c^4(3n^2-l^2-l)(2l-2)!}\ . \tag{3.5}$$

The error due to the last term would increase rapidly as n and l increase. The fact that our predictions for α_{N-1} do not vary significantly with n or l is an indication that Δ is quite small for most cases. The exception appears to be Kr II where α_{N-1} predicted does increase rather significantly when we go from $(l,n)=(3,4)$ to (3,6). Using the values in Table IV we get $\Delta\approx57$ cm^{-1}. This also means that $\alpha_{N-1}^{\rm exact}$ is a little smaller for Kr II,

$$\alpha_{N-1}^{\rm exact}\approx9.6\ , \tag{3.6}$$

which is the value we have suggested in Table V.

One may reverse the arguments to state that if we have reliable values for $\Delta\chi$ and α_{N-1}, Eq. (2.28) gives a one-parameter description of all the high-angular-momentum Rydberg energies of all halogen and inert-gas isoelectronic sequences. A satisfactory description is obtained for $A=3.9$. In particular we note that for large n, we have a quantum defect

$$\delta(J,K,l)=-A(\Delta\chi)f(J,K,l)\frac{8Z_c(2l-1)!}{(2l+2)!}+\alpha_{N-1}\frac{24Z_c^2(2l-2)!}{(2l+3)!},\quad n\gg l\gg1\ . \tag{3.7}$$

TABLE VIII. The average values of $A\Delta\chi$ obtained from solutions to Eq. (2.28) for (l,n) states, their average value $\overline{A\Delta\chi}$, average value of $\Delta\chi$ taking $A=3.9$ along with the predictions of HF calculations from Ref. [11], where $\Delta\chi=\chi_{N-1}-\chi_{N-3}$.

l,n	Ne I	Ar I	Kr I	Xe I	Ca III	Sc IV	Rb II	Sr III
3,4	2.04	5.14	6.86	8.42				
5	2.05	5.24	6.54	9.17				
6	1.97	4.94	6.69	9.34				
7	2.11	5.08	6.73	9.40				
8	1.97	4.94	6.45	9.80				
9	1.99	6.07	7.32	9.82				
4,5	2.03	5.19			3.09	2.54	5.21	4.43
6					3.10	2.58	4.97	4.39
7					3.21		5.46	4.61
8							5.66	
5,6						2.51		4.35
7						2.44		
6,7						2.50		
$\overline{A\Delta\chi}$	2.02	5.23	6.77	9.33	3.13	2.51	5.32	4.45
$\overline{\Delta\chi}$	0.52	1.34	1.75	2.41	0.80	0.64	1.36	1.14
$(\Delta\chi)^{\rm HF}$	0.52	1.35	1.78	2.50	0.75		1.37	1.10

Using the values of $A(\Delta\chi)$ and α_{N-1} given in the tables and the expression for $f(J,K,l)$ in Eqs. (1.5) and (1.6), this expression allows us to obtain the quantum defect for halogen isoelectronic sequences. For example, for Cl I, this expression gives

$$\delta(2,4,3)=0.0223\ , \tag{3.8}$$

whereas the experimental value of $-\delta E=9.7\ \text{cm}^{-1}$ for $J=2$, $K=4$, $l=3$, $n=8$ gives

$$\delta^{\text{expt}}(2,4,3)=0.0224\ . \tag{3.9}$$

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