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Multipolar polarizabilities and Rydberg states

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We have calculated multipolar polarizabilities for several atoms and ions, using some semiclassical relations and incorporating the correct asymptotic behavior in the electronic densities. We have also obtained simple expressions for penetration energies and nonadiabatic corrections which simplify the analysis of Rydberg states.

I. INTRODUCTION

The response of an atom or ion to a weak, static electric field is described in terms of its multipolar polarizabilities \( \alpha_L \) given by (in atomic units)

\[
\alpha_L = 2 \sum_i \frac{\langle 0 | \sum_j r_j^L \cos \theta_j | k \rangle^2}{E_k - E_0}.
\]  

(1.1)

They are important in the scattering of electrons by atoms and ions, in the calculation of van der Waals constants, and play a decisive role in determining the energies of Rydberg states of atoms and ions.

A. A brief review

The state of experimental and theoretical progress in the determination of dipolar \( (L = 1) \) polarizabilities has been comprehensively reviewed by Miller and Bederson. Here we only mention a few of the more recent theoretical efforts for calculating quadrupolar \( (L = 2) \) and higher multipolar polarizabilities.

Uncoupled Hartree–Fock equation has been used by Langhoff and Hurst, and Feiock and Johnson to obtain the multipolar polarizabilities of inert gases. The more elaborate coupled Hartree–Fock equation has been solved by Lahiri and Mukherji, and McEachran, Stauffer and Greita to calculate multipolar polarizabilities of inert gases and their isoelectronic sequences. Doran has used many-body perturbation theory and Mahan has used a generalized Sternheimer equation with a density dependent potential to evaluate multipolar polarizabilities of several inert gases and their isoelectronic sequences. Accurate values of the polarizabilities of alkali metals and alkaline earths have been deduced by using the effective quantum number approach.

The energies of Rydberg states are closely related to the multipolar polarizabilities of the core and hence provide an important source for deducing the polarizabilities. Particular mention must be made of the result obtained by Freeman and Kleppner for the quadrupolar polarizability of Na based on the experimental observation of energy levels of the Rydberg states of Na by Gallagher, Hill, and Edelstein.

B. An outline of our work

We present our analysis in two parts.

(a) We consider a function

\[
g_L(u) = \sum (E_k - E_0) \left| \frac{\langle 0 | \sum r_i \cos \theta_i | k \rangle^2}{\sum E_k} \right|
\]  

(1.2)

in terms of which one has

\[
\alpha_L = 2g_L(-1).
\]  

(1.3)

This function is relatively easy to evaluate for positive integers \( u = 0, 1, 2, \ldots \). While \( g_L(1) \) is particularly simple, \( g_L(0) \) is related to the one and two-particle probability densities. They are important in the scattering of electrons by atoms and ions, in the calculation of van der Waals constants, and play a decisive role in determining the energies of Rydberg states.

We use these expressions to predict the effective dipolar and quadrupolar polarizabilities to be used for describing the energies of Rydberg states,

\[
a_1^* = a_1 + \frac{3}{E_1} a_1,
\]  

(1.4)

\[
a_2^* = a_2 - \frac{3}{E_1} a_1,
\]  

(1.5)

where \( E_1 \) is the ionization energy of the core.

II. MULTIPOLAR POLARIZABILITIES

It is known that \( g_L(u) \) is relatively simple to evaluate for positive integers. Indeed for \( L = 1 \), it is trivially related to the well-known \( S(k) \) function which has been analyzed in great detail.

A. \( g_L(u) \) for \( u = 1 \) and 0

For \( u = 1 \), \( g_L(u) \) simplifies to

\[
g_L(1) = \frac{1}{2} L \left| \langle 0 | r_1^L - \frac{1}{2} | 0 \rangle \right|^2.
\]  

(2.1)

If \( L = 1 \), we obtain the Thomas–Reiche–Kuhn rule.

For \( u = 0 \), one has

\[
g_L(0) = \left| \langle 0 | \sum r_i^L \cos \theta_i | 0 \rangle \right|^2.
\]  

(2.2)
which in terms of the one-electron density \( \rho_i(r) \) and the two-electron density \( p_{12}(r,r') \) reduces to

\[
g_L(0) = \frac{1}{2L+1} \int \rho_i(r)r^{2L}d^3r + \int \rho_{12}(r,r')r^{2L}p_{12}(r,r')d^3r \quad . \tag{2.3}
\]

For simplifying the equation, we use the semiclassical two-electron density\(^{15}\)

\[
\rho_{12}(r,r') = \rho_i(r)\rho_i(r') - 2[F_{12}(r,r')]^2
\]

(2.4)

with

\[
\rho_i(r) = \frac{1}{2\pi^2\epsilon^2} \sum_l (2L + 1)k_l(r) , \tag{2.5}
\]

\[
F_{12}(r,r') = \frac{1}{4\pi^2\epsilon^2} \sum_l (2L + 1)P_l(\cos \theta)P_l(\cos \theta') \sin[k_l(R)(r-r')] , \tag{2.6}
\]

\[
k_l(R) = \left(2\phi - (l + 1/2)^2\right)^{1/2} , \tag{2.7}
\]

where \( \phi(r) \) is the effective potential and \( R = (r + r')/2 \). Proceeding along the same lines as in Refs. 15 and 21, leads to

\[
g_L(0) = \frac{1}{2L+1} \left[(1-f_L) \int \rho_i(r)r^{2L}d^3r , \right. \tag{2.8}
\]

\[
\left. + \sum_l (2L + 1)(2L' + 1) C_L(l,l') \right] \tag{2.9}
\]

\[
f_L = \frac{L_m}{L + 1} , \tag{2.10}
\]

where \( L_m \) is the highest value of \( l \) for the occupied states. The \( C_L \) elements are fairly simple for \( L = 2 \) and yield

\[
f_2 = \sum_l \frac{2l(4l^2 + 3l - 4)}{(2L + 3)} \left( \frac{2L - 1}{2L + 3} \right) \tag{2.11}
\]

For \( L = 3, 4 \), the expressions are complicated. They give

\[
f_L = 0 , \quad f_2 = \frac{2L}{7} , \quad f_3 = \frac{10}{63} , \quad f_4 = \frac{10}{63} , \quad f_L = 0 , \quad f_2 = \frac{2L}{7} , \quad f_3 = \frac{1}{2L+1} \tag{2.12}
\]

For obtaining \( g_L(0) \) in Eq. (2.8) we now only require an accurate estimation of \( \langle \rho^{2L} \rangle \)

\[
\langle \rho^{2L} \rangle = \int \rho_i(r)r^{2L}d^3r . \tag{2.13}
\]

B. Modified Thomas–Fermi equation

The value of \( \langle \rho^{2L} \rangle \) required for estimating \( g_L(0) \) depends quite sensitively on the large-\( r \) behavior of electron density which has the form\(^{22}\)

\[
\rho(r) \sim r^{-b} e^{-ar} , \quad \text{for } r > 1 , \tag{2.14}
\]

\[
a = (Z - N + 1) \left[ \frac{2}{E_i} \right]^{1/2} - 2 , \tag{2.15}
\]

\[
b = 2|2E_i|^{1/2} , \tag{2.16}
\]

where \( E_i \) is the ionization energy of the atom or ion, \( Z \) is the atomic number, and \( N \) is the number of electrons. We had recently proposed\(^{14,15}\) a modification of the Thomas–Fermi model which includes this asymptotic behavior and is described by the equation

\[
\frac{d^2\eta}{dr^2} = \frac{4}{3\pi} \frac{(2\eta)^{3/2}}{r^{1/2}} + Ar^a e^{-br} , \tag{2.17}
\]

where \( A \) and \( b \) are constants for a given atom or ion. The \( A \) and the asymptotic behavior in Eq. (2.17) and traces the solution to smaller values of \( r \) by using Eq. (2.16). We choose that value of \( A \) for which the condition in Eq. (2.18) is satisfied. The expression for \( \langle \rho^{2L} \rangle \) is then evaluated by using the density

\[
\rho_i(r) = \frac{1}{3\pi^2} \left( \frac{2\eta}{r} \right)^{3/2} + A \frac{r^a e^{-br}}{4\pi} \tag{2.18}
\]

which is obtained by solving Eq. (2.16). The value of \( A \) is very small and does not affect the results significantly.

C. Parametric form for \( g_L(\theta) \)

It was found\(^{15}\) that for \( \theta < 1 \), the main contribution to the summation over the intermediate states in Eq. (1.2) is from terms which correspond to \( E_k - E_i \) being equal to the ionization energy \( E_i \), and the average energy \( E_a \). We therefore, consider a parametrization

\[
g_L(\theta) = BE_i^* \frac{\epsilon}{\epsilon_i} + CE_i^* , \tag{2.19}
\]

where \( B \) and \( C \) are constants for a given atom or ion. The constants \( B \) and \( C \) are determined from the requirements

\[
g_L(0) = \frac{1}{2L+1} \left(1 - f_L \right) \langle \rho^{2L} \rangle , \tag{2.20}
\]

\[
g_L(1) = \frac{1}{2} \langle \rho^{2L-2} \rangle \tag{2.21}
\]

given in Eqs. (2.8) and (2.1). Determination of \( B \) and \( C \) allows us to obtain \( g_L(-1) \) and hence the multipolar polarizabilities \( \alpha_L \) as

\[
\alpha_L = \frac{1}{2L+1} \left[ \frac{1}{E_i} \right] \frac{1}{E_i} \left[ B(E_k + E_i)(1 - f_L)\langle \rho^{2L} \rangle \right. \tag{2.22}
\]

\[
- \frac{L(2L+1)}{2L+1} \langle \rho^{2L-2} \rangle \right] . \tag{2.23}
\]

In this expression, the first term inside the bracket is found to be dominant. Therefore, since the average energy \( E_a \) is much larger than the ionization energy \( E_i \), the expression for \( \alpha_L \) is rather insensitive to \( E_i \), which may be estimated\(^{15}\) from Coulombic levels with suitable screening. The dependence of \( \alpha_L \) on \( E_i \) however, is sensitive. This is not surprising since the

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outer electrons play a major role in determining polarizability and susceptibility of atoms.

### D. Multipolar polarizabilities

We have calculated the multipolar polarizabilities for several atoms and ions using the expression in Eq. (2.23). The dipolar polarizability and susceptibilities required for the evaluation of \( \langle \rho^2 \rangle \) are taken from Table 9 and Table 14 of atoms. Eq. (2.19). We prefer to present the results in terms of the dipolar polarizability and

\[
R_{L+1, L} = \frac{\alpha_{L+1}}{\alpha_L}.
\]  

(2.24)

**Table I.** Calculated values of diamagnetic susceptibility and multipolar polarizabilities \( R_{21} = \alpha_2/\alpha_1, R_{32} = \alpha_3/\alpha_2, R_{43} = \alpha_4/\alpha_3 \), for some atoms and their isoelectronic sequences, along with some experimental values (\( a \) = Ref. 26, \( b \) = Ref. 1, \( c \) = Ref. 29, \( d \) = Ref. 25) and some values obtained from theoretical calculations (\( A \) = Ref. 7, \( B \) = Ref. 5, \( C \) = Ref. 24, \( D \) = Ref. 4, \( E \) = Ref. 27, \( F \) = Ref. 28, and \( H \) = Ref. 6).

<table>
<thead>
<tr>
<th>N/Z</th>
<th>( E_i(E_a) )</th>
<th>( A )</th>
<th>( \chi )</th>
<th>( \alpha_1 )</th>
<th>( R_{21} )</th>
<th>( R_{32} )</th>
<th>( R_{43} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>10/10</td>
<td>0.793 ( (12.7) )</td>
<td>44.0</td>
<td>1.61</td>
<td>3.32</td>
<td>3.43</td>
<td>8.19</td>
<td>9.96</td>
</tr>
<tr>
<td>10/11</td>
<td>1.74 ( (15.9) )</td>
<td>179</td>
<td>1.14</td>
<td>1.09</td>
<td>1.91</td>
<td>4.41</td>
<td>5.08</td>
</tr>
<tr>
<td>10/12</td>
<td>2.95 ( (19.5) )</td>
<td>530</td>
<td>0.84</td>
<td>0.48</td>
<td>1.26</td>
<td>2.85</td>
<td>3.20</td>
</tr>
<tr>
<td>10/13</td>
<td>4.41 ( (23.4) )</td>
<td>( 1.31 \times 10^4 )</td>
<td>0.66</td>
<td>0.259</td>
<td>0.90</td>
<td>2.02</td>
<td>2.22</td>
</tr>
<tr>
<td>10/15</td>
<td>8.10 ( (32.3) )</td>
<td>5.63 ( 10^6 )</td>
<td>0.44</td>
<td>0.098</td>
<td>0.53</td>
<td>1.18</td>
<td>1.27</td>
</tr>
<tr>
<td>10/16</td>
<td>10.33 ( (37.3) )</td>
<td>1.02 ( 10^4 )</td>
<td>0.36</td>
<td>0.063</td>
<td>0.42</td>
<td>0.95</td>
<td>1.00</td>
</tr>
<tr>
<td>10/18</td>
<td>15.48 ( (48.3) )</td>
<td>2.89 ( 10^4 )</td>
<td>0.268</td>
<td>0.0323</td>
<td>0.29</td>
<td>0.66</td>
<td>0.69</td>
</tr>
<tr>
<td>17/17</td>
<td>0.478 ( (26.6) )</td>
<td>21.0</td>
<td>3.9</td>
<td>15.7</td>
<td>5.82</td>
<td>14.4</td>
<td>18.2</td>
</tr>
<tr>
<td>18/18</td>
<td>0.579 ( (28.8) )</td>
<td>35.5</td>
<td>3.51</td>
<td>11.3</td>
<td>4.61</td>
<td>11.1</td>
<td>14.4</td>
</tr>
<tr>
<td>18/19</td>
<td>1.17 ( (32.6) )</td>
<td>120</td>
<td>2.90</td>
<td>4.66</td>
<td>3.00</td>
<td>6.98</td>
<td>8.32</td>
</tr>
<tr>
<td>18/20</td>
<td>1.88 ( (36.6) )</td>
<td>342</td>
<td>2.42</td>
<td>2.45</td>
<td>2.25</td>
<td>4.90</td>
<td>5.70</td>
</tr>
<tr>
<td>18/22</td>
<td>3.67 ( (45.6) )</td>
<td>1.88 ( 10^3 )</td>
<td>1.78</td>
<td>0.94</td>
<td>1.37</td>
<td>2.90</td>
<td>3.24</td>
</tr>
<tr>
<td>18/27</td>
<td>10.10 ( (72.2) )</td>
<td>4.13 ( 10^4 )</td>
<td>0.99</td>
<td>0.20</td>
<td>0.62</td>
<td>1.24</td>
<td>1.33</td>
</tr>
<tr>
<td>35/35</td>
<td>0.435 ( (72.8) )</td>
<td>24.2</td>
<td>7.1</td>
<td>20.8</td>
<td>6.35</td>
<td>16.4</td>
<td>23.8</td>
</tr>
<tr>
<td>36/36</td>
<td>0.515 ( (75.5) )</td>
<td>40.0</td>
<td>6.34</td>
<td>15.6</td>
<td>5.19</td>
<td>13.3</td>
<td>19.4</td>
</tr>
<tr>
<td>36/37</td>
<td>1.011 ( (80.5) )</td>
<td>124</td>
<td>5.50</td>
<td>6.9</td>
<td>3.63</td>
<td>8.50</td>
<td>11.8</td>
</tr>
<tr>
<td>36/38</td>
<td>1.61 ( (85.7) )</td>
<td>340</td>
<td>4.83</td>
<td>3.81</td>
<td>2.81</td>
<td>5.92</td>
<td>8.21</td>
</tr>
<tr>
<td>53/53</td>
<td>0.384 ( (130.0) )</td>
<td>19.9</td>
<td>10.1</td>
<td>34.1</td>
<td>7.01</td>
<td>18.9</td>
<td>27.7</td>
</tr>
<tr>
<td>54/54</td>
<td>0.446 ( (133.3) )</td>
<td>32.4</td>
<td>9.14</td>
<td>26.5</td>
<td>5.87</td>
<td>15.7</td>
<td>23.0</td>
</tr>
<tr>
<td>54/55</td>
<td>0.923 ( (138.8) )</td>
<td>114</td>
<td>7.83</td>
<td>11.0</td>
<td>3.92</td>
<td>9.44</td>
<td>13.2</td>
</tr>
<tr>
<td>54/56</td>
<td>1.50 ( (144.7) )</td>
<td>343</td>
<td>6.85</td>
<td>5.9</td>
<td>2.90</td>
<td>6.67</td>
<td>8.95</td>
</tr>
</tbody>
</table>
The reason for this is that the possible errors due to the choice of \( E_p \) as a characteristic energy, and the choice of the correction term in Eq. (2.16) are minimized when we take ratios of polarizabilities.

In Table I, we have given the results for some atoms and their isoelectronic sequences, along with some experimental numbers and some numbers from other calculations. The values predicted\(^5\) for dipolar polarizabilities are generally in good agreement with the experimental values. For higher polarizabilities, there are no reliable experimental values with the exception of the empirical values of Freeman and Kleppner\(^7\) who predict a value of \( \alpha = 0.998 \) and \( \alpha = 1.91 \) for Ne\(^+\), which gives

\[
R_{21} = 1.914
\]  
(2.25)

and this compares very favorably with our prediction of \( R_{21} = 1.91 \). For other atoms and ions of the inert gas isoelectronic sequences, we have compared our results with the calculations of Mahan\(^7\) using density dependent potentials, McCracken et al.\(^3\) and Lahiri and Mukherji\(^4\) using coupled Hartree–Fock equations, and Doran\(^6\) using many-body perturbation theory. While the agreement between different sets of numbers is reasonable, there are some significant differences. We would like to propose a test for estimating the reliability of the different calculations.

**E. Large-\(L\) multipolar polarizabilities**

The polarizabilities depend very sensitively on the large-\(r\) behavior of electronic densities. This is particularly so for high order multipolar polarizabilities.

If the correct asymptotic behavior given in Eq. (2.15) is incorporated in the electronic densities, it will dominate the evaluation of \( \langle r^{2L} \rangle \) for large \( L \). Using the expression in Eq. (2.15) as the leading term in the asymptotic region, one then obtains

\[
\frac{\langle r^{2L} \rangle}{\langle r^2 \rangle} = \frac{(a + 2L + 3)(a + 2L + 4)}{b^2} \quad \text{for } L \to \infty ,
\]  
(2.26)

where \( a \) and \( b \) are defined in Eq. (2.15). We would like to suggest that a reliable calculation of \( \alpha_L \) must satisfy this condition at least approximately. A pertinent point would be the value of \( L \) for which one may be expected to be close to the value in Eq. (2.26). We find that for \( L = 3 \), our values of the ratio are 12.84 and 25.10 for Ne and Xe, respectively, close to the corresponding limiting values of 12.98 and 25.85. We therefore, suggest that a reliable approach to the calculation of multipolar polarizabilities should give a value for \( \langle r^0 \rangle / \langle r^2 \rangle \) which agrees with the limiting value in Eq. (2.26) to within about 5%.

We can also obtain a simple expression for the ratio of polarizabilities for large \( L \), by noting that the second term in Eq. (2.23) is unimportant for ratios. Using Eq. (2.26), we get

\[
\frac{\alpha_{L+1}}{\alpha_L} \approx \frac{(a + 2L + 3)(a + 2L + 4)(2L + 1)(1 - f_{L+1})}{b^2(2L + 3)(1 - f_L)},
\]  
(2.27)

where \( f_L \) are given in Eqs. (2.11) to (2.13). For \( L = 2 \), the expression on the right-hand side gives 8.04, 11.87, 14.17, 17.00 for Ne, Ar, Kr, and Xe, respectively, whereas the corresponding values for the left-hand side calculated from Eq. (2.23) are 8.19, 11.1, 13.3, and 15.7. For higher values of \( L \), the limiting values may be expected to be essentially those obtained from Eq. (2.23).

Whatever the approach, we feel that a reliable calculation of multipolar polarizabilities of atoms and ions must incorporate the asymptotic behavior given in Eq. (2.15), and if it does, its predictions should be close to the limiting values in Eq. (2.27) for \( L > 2 \).

**III. ENERGIES OF RYDBERG STATES**

Rydberg states provide an important source of information about polarizabilities since their energies differ from the hydrogenic energies mainly due to the polarization potential.\(^12,24\) We consider two pertinent points: (i) Energy due to the penetration of the wave function of the excited electron into the core, which is usually calculated numerically by using densities obtained from complicated many-electron calculations. We provide a simple analytic expression for this energy. (ii) Nonadiabatic corrections for which we deduce a simple perturbative expression.

**A. Penetration energy**

The first order penetration energy is given by

\[
E_{pen} = \int \rho(r) \left[ \frac{1}{|R - r|} - \frac{1}{R} \right] |\Psi(R)|^2 d^3r d^3R ,
\]  
(3.1)

where \( \rho(r) \) is the density of the core electrons and \( \Psi(R) \) is the hydrogenic wave function of the outer electron. Using Fourier transforms of \( 1/R \) and \( 1/(R - r) \) terms, one gets

\[
E_{pen} = \frac{1}{2\pi^2} \int d^3R \left| \Psi(R) \right|^2 \int d^3k \frac{1}{k^2} e^{i\mathbf{kr}}
\]  
\[ \times \int d^3r \rho(r) |e^{i\mathbf{kr}} - 1| . \]
(3.2)

The value of the last integral is \(-N \) for large \( k \), and \(-\xi(\mathbf{r}) k^3 \) for small \( k \). We therefore, use an approximation

\[
\int d^3r \rho(r) |e^{i\mathbf{kr}} - 1| \approx -N - k^2 \mathbf{r}^2 \frac{6N}{6N + k^2 \mathbf{r}^2} ,
\]  
(3.3)

which has the required behavior for both small and large \( k \). This leads to a core potential

\[
V_{core}(R) = -N \frac{e^{-K/d}}{R} ,
\]  
(3.4)

\[
d = \left[ \langle \mathbf{r}^2 \rangle / 6N \right]^{1/2} ,
\]

and a penetration energy

\[
E_{pen} = -N \left[ \langle n' + 1 \rangle \langle 2l + 1 \rangle \langle \mathbf{r}^2 \rangle \right]^{1/2} \frac{2l^2 - 1}{n'^2(2l + 1)(1 + 2d/n'^2)}
\]  
\[ \times F \left( -n', -n', 2l + 2, 4d^2 / n'^2 \right) , \]
(3.5)

where \( n', l \) are the quantum numbers of the outer electron, \( n' = n - l - 1 \), and \( F \) is the hypergeometric function.

For the evaluation of \( E_{pen} \) in Eq. (3.5) one only needs \( \langle \mathbf{r}^2 \rangle \) which is equal to 6\( \mathbf{r} \) where \( \mathbf{r} \) is the diamagnetic susceptibility of the core. It may either be taken from experimental values of \( \chi \), which however, are not accurately known for...
ions, or calculated using the density in Eq. (2.19). The values predicted for \( E_{\text{pen}} \) by Eq. (3.5) are in fairly good agreement with the value used by Freeman and Kleppner\(^2\) for Na. For Na with \( n = 13, l = 3 \), they get \( E_{\text{pen}} \approx 30.3 \pm 10 \) MHz whereas with \( \chi = 1 \), we get a value of \( E_{\text{pen}} \approx 42 \) MHz. One can also obtain quantum defect \( \delta_{\text{pen}} \) from Eq. (3.5) for large \( n \),

\[
\delta_{\text{pen}} = N \left( \frac{2d}{2l+1} \right)^{2l+1} \cdot e^{-4d} .
\]

(3.6)

For the \( l = 3 \) state of Na, this expression gives a value of about \( 1.4 \times 10^{-5} \) for \( \chi \approx 1 \), whereas the value obtained by Freeman and Kleppner\(^2\) is about \( 1.0 \times 10^{-5} \). Considering the uncertainties involved in both the estimations, the agreement between the two numbers is reasonable.

### B. Nonadiabatic corrections

Nonadiabatic corrections to the energies can be incorporated by including the states of the outer electron in the summation over the intermediate states of higher order Born terms.

The second order Born term is

\[
\delta E^{(2)} = \sum_{p,j} \left| \frac{(0,0)V(R,r;)[p,j]}{E_0 - E_p + \epsilon_0 - \epsilon_j} \right|^2 ,
\]

(3.7)

where \( p \) are the core states with energies \( E_p, j \) are the outer electron states with energies \( \epsilon_j \), and

\[
V(R,r;)_p = \sum \left( \frac{1}{|R - r_j|} - \frac{1}{R} \right) .
\]

(3.8)

For \( E_p = E_0 \) one gets the second order Born term for the potential in Eq. (3.4). Since the first order contribution given in Eq. (3.5) is very small, we neglect the second order contributions from terms with \( E_p \neq E_0 \). For \( E_p = E_0 \), one may expand the denominator of Eq. (3.7) to get

\[
\delta E^{(2)} \approx \sum_{p,j} \left| \frac{(0,0)V(R,r;)[p,j]}{E_0 - E_p + \epsilon_0 - \epsilon_j} \right|^2 \times \left( 1 - \frac{1}{E_0 - E_p + \epsilon_0 - \epsilon_j} + \ldots \right) .
\]

(3.9)

The first term inside the bracket leads to the usual adiabatic potential. The second term is the leading correction due to nonadiabatic effects.

For estimating the contribution of the second term inside the bracket, we expand \( V(R,r;)_p \) and retain the leading term for large \( R \),

\[
V(R,r;)_p \approx \sum \frac{R r_j}{R^3} .
\]

(3.10)

Then the nonadiabatic term \( \delta E_{\text{na}} \) is given by

\[
\delta E_{\text{na}} = \sum_{p,j} (\epsilon_j - \epsilon_0) \left| \frac{\langle 0 | \frac{R r_j}{R^3} | 1 \rangle \langle 1 | \sum_r r_j | p \rangle}{(E_0 - E_p)^2} \right|^2 .
\]

(3.11)

Taking \( \epsilon_j - \epsilon_0 \) inside and replacing it by the Hamiltonian, we obtain, after some simplification

\[
\delta E_{\text{na}} = 3 \left| \frac{1}{R^6} \right| \sum_p \left| \frac{\langle 0 | \sum_r P_i | \cos \theta | r_j | p \rangle}{(E_0 - E_p)^2} \right|^2 .
\]

(3.12)

In terms of \( g_L(u) \) defined in Eq. (1.2) this expression is

\[
\delta E_{\text{na}} = 3g_1(-2) \left| \frac{1}{R^6} \right| 0 \rangle .
\]

(3.13)

An expression for \( g_1(-2) \) can be obtained from Eqs. (2.20), (2.21), and (2.22) to give us

\[
\delta E_{\text{na}} = 3 \left( \frac{1}{R^6} \right) 0 \rangle \times \frac{2(1 - f_1^2) E_a^2 + E_a E_r + E_r^2 \langle 2^2 \rangle - 3N (E_a + E_r)}{6E_a^2 E_r^2} .
\]

(3.14)

Numerically it is found that to a high accuracy,

\[
g_1(-2) = g(-1)/E_r
\]

so that

\[
\delta E_{\text{na}} = 3 \left( \frac{1}{2E_r} \right) \alpha_1 \left| \frac{1}{R^6} \right| 0 \rangle .
\]

Combining this term with the adiabatic terms, we finally get, for the second order energy,

\[
\delta E^{(2)} \approx \left( \frac{1}{2} \right) \left( \alpha_1 \left| \frac{1}{R^6} \right| 0 \rangle + \left( \alpha_2 - \frac{3}{E_r} \alpha_1 \right) \left| \frac{1}{R^6} \right| 0 \rangle \right) .
\]

(3.16)

In our description therefore, the effective dipolar and quadrupolar polarizabilities are

\[
\alpha_1' = \alpha_1 ,
\]

(3.17)

\[
\alpha_2' = \alpha_2 - \frac{3}{E_r} \alpha_1 .
\]

(3.18)

The predictions of our expression are in reasonable agreement with the predictions of Eissa and Opik\(^23\) for Na\(^+\), Mg\(^2+\), K\(^+\) and Ca\(^{2+}\). The results may be presented in terms of \( y_11, y_22, \) and \( y_21 \) where

\[
y_11 = y_1 \alpha_1 ,
\]

(3.19)

\[
y_22 = y_2 \alpha_2 + y_2 \alpha_1 .
\]

While Eissa and Opik predict values close to 1 for \( y_11, y_22, \) our values are precisely 1. For \( y_21 \), Eissa and Opik predict values \(-1.41, -1.01, -2.80, -2.17\) for Na\(^+\), Mg\(^2+\), K\(^+\), Ca\(^{2+}\), respectively, with the outer electron in the \( 4f \) state whereas our predictions are \(-1.72, -1.02, -2.56, -1.60\), respectively. The agreement between the two sets of numbers is reasonable.

There is rather a wide range of values for effective quadrupolar polarizabilities for Cs\(^+\) deduced empirically, ranging from a value\(^25\) of about 38 to 184. Taking \( \alpha_1 = 15.5 \) we get from Eq. (3.18),

\[
\alpha_2' = 10.6 \quad \text{for} \quad \alpha_2 = 61.0 ,
\]

(3.20)

\[
= 52.6 \quad \text{for} \quad \alpha_2 = 103.0 .
\]

Since the values of \( \alpha_2 \) used in these two cases are the lowest and the highest of the calculated values (see Table I), our analysis supports the lower observed values\(^25\) for the effective quadrupolar polarizability in Cs\(^+\). A similar analysis can be carried out using Eq. (3.18) for K\(^+\) and Rb\(^+\). For K\(^+\), we predict \( \alpha_2 = 2.2 \) (with \( \alpha_1 = 5.0 \) and \( \alpha_2 = 15 \)) and for Rb\(^+\) we predict \( \alpha_2 = 9.3 \) (with \( \alpha_1 = 9.0 \) and \( \alpha_2 = 36 \)). However, adequate empirical analysis has not been carried out for these cases with high \( l \) excitations of the outer electron.
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