

Rydberg States of ThIII and UV

W. R. Johnson

Department of Physics, Notre Dame University

June 25, 2003

Abstract

We examine the Rydberg spectrum of the two actinide ions Th^{2+} and U^{5+} . The states of interest consist of a weakly bound electron interacting with the $5F_{5/2}$ ground states of the respective one electron ions. First- and second-order correlation corrections are worked out.

1 Basic Assumptions

We consider an $N+1$ electron with atom with one electron in a high Rydberg state. We neglect the exchange interaction between the Rydberg electron and the N -electron ion. The Hamiltonian of the atom is written

$$H = H_N(\vec{r}_1 \cdots \vec{r}_N) + h(\vec{r}) + U(\vec{r}, \vec{r}_1 \cdots \vec{r}_N), \quad (1)$$

where H_N is the Hamiltonian of the N -electron ion, h is the Rydberg electron:

$$h(\vec{r}) = T + V_{\text{nuc}}(r) + \frac{N}{r}, \quad (2)$$

and U is the interaction Hamiltonian,

$$U(\vec{r}, \vec{r}_1 \cdots \vec{r}_N) = \sum_{i=1}^N \frac{1}{|\vec{r} - \vec{r}_i|} - \frac{N}{r} \quad (3)$$

$$= \sum_{L=1}^{\infty} \sum_{M=-L}^L \frac{C_{LM}(\hat{r})}{r^{L+1}} \sum_{i=1}^N r_i^L C_{LM}^*(\hat{r}_i). \quad (4)$$

In the expansion of the interaction Hamiltonian, we assume that the Rydberg electron wave-function has no overlap with the ionic core.

In lowest-order, the atomic wave function may be written

$$\Psi_0 = \Phi_0(\vec{r}_1 \cdots \vec{r}_N) \phi_k(\vec{r}), \quad (5)$$

where

$$H_N(\vec{r}_1 \cdots \vec{r}_N) \Phi_n(\vec{r}_1 \cdots \vec{r}_N) = E_n \Phi_n(\vec{r}_1 \cdots r_N) \quad (6)$$

$$h(\vec{r}) \phi_l(\vec{r}) = \epsilon_l \phi_l(\vec{r}). \quad (7)$$

The lowest-order energy of a Rydberg state is $E_0 + \epsilon_k$.

2 First-Order Energy

The ground state of both of the $N = 87$ electron ions, Th^{3+} and U^{5+} , is a $J_0 = 5/2$ state with a $5f_{5/2}$ valence electron outside a Rn-like core. The two valence electron systems of interest here have a Rydberg electron with angular momentum $(j_k m_k)$ coupled to the $(J_0 M_0)$ ground-state to give a coupled two-electron state (FM_F) . We use the notation of hyperfine structure here, because of the similarity of the present analysis to the analysis of hyperfine interactions.

The first-order energy is

$$E_F^{(1)} = \langle (J_0 M'_0, km'_k) FM_F | U | (J_0 M_0, km_k) FM_F \rangle \quad (8)$$

$$= \langle J_0 M'_0, km'_k | FM_F \rangle \langle J_0 M_0, km_k | FM_F \rangle \times$$

$$\sum_{LM} (-1)^M \langle km'_k | \frac{C_{LM}(\hat{r})}{r^{L+1}} | km_k \rangle \langle J_0 M'_0 | \sum_i C_{L-M}(\hat{r}_i) r_i^L | J_0 M_0 \rangle. \quad (9)$$

Carrying out the sums over magnetic quantum numbers, we find

$$E_F^{(1)} = \sum_{L=2,4} (-1)^{J_0+k+F} \left\{ \begin{matrix} J_0 & k & F \\ k & J_0 & L \end{matrix} \right\} \times \langle k || C_L || k \rangle \left\langle \frac{1}{r^{L+1}} \right\rangle_k \langle J_0 || \sum_i C_L(\hat{r}_i) r_i^L || J_0 \rangle. \quad (10)$$

Only two terms $L=2$ and $L=4$ contribute for the cases of interest where $J_0 = 5/2$. In the HF approximation, the core parameters $\langle F_{5/2} || \sum_i r_i^L C_L(\hat{r}_i) || F_{5/2} \rangle$ are found to be:

Ion	$\langle F_{5/2} r^2 C_2 F_{5/2} \rangle$	$\langle F_{5/2} r^4 C_4 F_{5/2} \rangle$
Th^{3+}	-3.755	15.97
U^{5+}	-2.207	4.718

3 Second-Order Energy

The second-order energy is

$$\Delta E^{(2)} = - \sum_{(nl) \neq (0k)} \frac{\langle 0k|U|nl\rangle \langle nl|U|0k\rangle}{E_n - E_0 + \epsilon_k - \epsilon_l} \quad (11)$$

$$\begin{aligned} &= - \sum_{n \neq 0, \text{all } l} \frac{\langle 0k|U|nl\rangle \langle nl|U|0k\rangle}{E_n - E_0 + \epsilon_k - \epsilon_l} \\ &\quad - \sum_{l \neq k} \frac{\langle 0k|U|0l\rangle \langle 0l|U|0k\rangle}{\epsilon_k - \epsilon_l}. \end{aligned} \quad (12)$$

We expand the denominator in the first term of Eq. (12) as

$$\frac{1}{E_n - E_0 + \epsilon_l - \epsilon_k} = \frac{1}{E_n - E_0} + \frac{\epsilon_k - \epsilon_l}{(E_n - E_0)^2} + \frac{(\epsilon_k - \epsilon_l)^2}{(E_n - E_0)^3} + \dots$$

to find

$$\begin{aligned} \Delta E^{(2)} &= - \left\langle k \left| \sum_{n \neq 0} \frac{\langle 0|U|n\rangle \langle n|U|0\rangle}{E_n - E_0} \right| k \right\rangle \\ &\quad - \left\langle k \left| \sum_{n \neq 0} \frac{\langle 0|[h, U]|n\rangle \langle n|U|0\rangle}{(E_n - E_0)^2} \right| k \right\rangle + \dots \\ &\quad - \sum_{l \neq k} \frac{\langle 0k|U|0l\rangle \langle 0l|U|0k\rangle}{\epsilon_k - \epsilon_l}. \end{aligned} \quad (13)$$

3.1 Polarizability correction

In this subsection, we examine the first term in Eq. (13), which leads to the correction to the energy of the Rydberg state from the core polarizability. We have

$$\begin{aligned} \Delta E_{\text{pol}}^{(2)} &= - \langle J_0 M'_0, k m'_k | F M_F \rangle \langle J_0 M_0, k m_k | F M_F \rangle \times \\ &\quad \sum_{L' M'_L} \sum_{L M_L} \left\langle k m'_k \left| \frac{C_{L' M'_L}(\hat{r}) C_{L M_L}^*(\hat{r})}{r^{L+L'+2}} \right| k m_k \right\rangle \times \\ &\quad \sum_{n \neq 0} \frac{\langle J_0 M'_0 | \sum_i r_i^{L'} C_{L' M'_L}^* | J_n M_n \rangle \langle J_n M_n | \sum_j r_j^L C_{L M_L} | J_0 M_0 \rangle}{E_n - E_0} \end{aligned} \quad (14)$$

We expand the product of two spherical tensors as

$$C_{L' M'_L}(\hat{r}) C_{L M_L}^*(\hat{r}) = \sum_{J M_J} A_{J M_J} C_{J M_J}(\hat{r}), \quad (15)$$

and find

$$A_{JM_J} = \frac{[J]}{\sqrt{[L][L']}} \langle L'M'_L | C_{JM_J} | LM_L \rangle. \quad (16)$$

Therefore,

$$C_{L'M'_L}(\hat{r}) C_{LM_L}^*(\hat{r}) = \sum_{JM_J} \frac{[J]}{\sqrt{[L][L']}} \langle L'M'_L | C_{JM_J} | LM_L \rangle C_{JM_J}(\hat{r}). \quad (17)$$

It follows that

$$\begin{aligned} \left\langle km'_k \left| \frac{C_{L'M'_L}(\hat{r}) C_{LM_L}^*(\hat{r})}{r^{L+L'+2}} \right| km_k \right\rangle &= \sum_{JM_J} \frac{[J]}{\sqrt{[L][L']}} \times \\ &\langle L'M'_L | C_{JM_J} | LM_L \rangle \langle km'_k | C_{JM_J} | km_k \rangle \left\langle \frac{1}{r^{L+L'+2}} \right\rangle_k, \end{aligned} \quad (18)$$

Carrying out the sums over magnetic quantum numbers, we find

$$\begin{aligned} \Delta E_{\text{pol}}^{(2)} &= \sum_J (-1)^{J_0+k+F} \left\{ \begin{array}{ccc} J_0 & k & F \\ & k & J_0 & J \end{array} \right\} [J] \langle k || C_J || k \rangle \times \\ &\sum_{L'} \frac{1}{\sqrt{[L][L']}} \langle L' || C_J || L \rangle \left\langle \frac{1}{r^{L+L'+2}} \right\rangle_k \\ &\sum_{n \neq 0} (-1)^{L'} \left\{ \begin{array}{ccc} L' & L & J \\ J_0 & J_0 & J_n \end{array} \right\} \frac{\langle J_0 || \sum_i r_i^{L'} C_{L'} || J_n \rangle \langle J_n || \sum_j r_j^L C_L || J_0 \rangle}{E_n - E_0}. \end{aligned} \quad (19)$$

For the $5F_{5/2}$ state of interest here, $J_0=5/2$ and $J < 2J_0 = 5$; moreover, J is even. It follows that $J = 0, 2, 4$.

3.1.1 Contribution of $J = 0$

In the following, we include only those terms with $L + L' \leq 4$. If we set $J = 0$ in Eq. (19), then we find

$$\Delta E_0^{(2)} = -\frac{1}{2} \left\langle \frac{\bar{\alpha}_1}{r^4} \right\rangle_k - \frac{1}{2} \left\langle \frac{\bar{\alpha}_2}{r^6} \right\rangle_k, \quad (20)$$

where $\bar{\alpha}_1$ and $\bar{\alpha}_2$ are the scalar parts of the dipole and quadrupole polarizabilities, respectively. The scalar polarizabilities are defined by

$$\bar{\alpha}_L = \frac{2}{[L][J_0]} \sum_n \frac{\left| \langle J_n || \sum_j r_j^L C_L || J_0 \rangle \right|^2}{E_n - E_0}. \quad (21)$$

3.1.2 Contribution from $J = 2, 4$

The $J = 2$ and 4 terms in Eq. (19) consists of partial contributions from all $L > 1$. The corresponding values of L' have the same parity as L and satisfy $\max(1, |L - J|) \leq L' \leq L + J$.

Terms with $L = L' = 1$: We consider the $L = L' = 1$ term first. This term arises only for $J = 0$ and 2. We have already evaluated the $J = 0$ part. The $J = 2, L = L' = 1$ term can be rewritten in terms of the $L = 1$ tensor polarizability

$$\alpha_{1t} = 4\sqrt{\frac{5}{6}} \begin{pmatrix} J_0 & 2 & J_0 \\ -J_0 & 0 & J_0 \end{pmatrix} \sum_{J_n} (-1)^{J_0+J_n} \begin{Bmatrix} 1 & 1 & 2 \\ J_0 & J_0 & J_n \end{Bmatrix} \frac{|\langle J_n || \sum_j r_j C_1 || J_0 \rangle|^2}{E_n - E_0}. \quad (22)$$

We note in passing that

$$\begin{pmatrix} J_0 & 2 & J_0 \\ -J_0 & 0 & J_0 \end{pmatrix} = \sqrt{\frac{J_0(2J_0 - 1)}{(J_0 + 1)(2J_0 + 1)(2J_0 + 3)}}. \quad (23)$$

Substituting into Eq. (19), we find that the $L = L' = 1$ contribution to the $J = 2$ term is:

$$\Delta E_2^{(2)} \Big|_{11} = -\frac{1}{2} (-1)^{J_0+k+F} \begin{Bmatrix} J_0 & k & F \\ k & J_0 & 2 \end{Bmatrix} \langle k || C_2 || k \rangle \begin{pmatrix} J_0 & 2 & J_0 \\ -J_0 & 0 & J_0 \end{pmatrix}^{-1} \left\langle \frac{\alpha_{1t}}{r^4} \right\rangle_k. \quad (24)$$

There are no further second-order corrections falling off as $1/r^4$.

Terms with $L = L' = 2$: The $J > 0$ terms with $L = L' = 2$ can be summarized as

$$\begin{aligned} \Delta E_2^{(2)} \Big|_{22} = & - \sum_{J=2,4} (-1)^{J_0+k+F} \begin{Bmatrix} J_0 & k & F \\ k & J_0 & J \end{Bmatrix} \langle k || C_J || k \rangle \left\langle \frac{1}{r^6} \right\rangle_k \times \\ & \langle 2 || C_J || 2 \rangle \sum_{J_n} (-1)^{J_0+J_n} \begin{Bmatrix} 2 & J_0 & J_n \\ J_0 & 2 & J \end{Bmatrix} \frac{|\langle J_n || \sum_j r_j^2 C_2 || J_0 \rangle|^2}{E_n - E_0}. \end{aligned} \quad (25)$$

For the record, we note that

$$\langle 2 || C_2 || 2 \rangle = -\frac{\sqrt{70}}{7} \quad \text{and} \quad \langle 2 || C_4 || 2 \rangle = \frac{\sqrt{70}}{7}.$$

Terms with $L = 1, 3$ and $L' = 3, 1$: The sum of the terms with $L = 1, 3$ and $L' = 3, 1$ can be written

$$\Delta E_2^{(2)} \Big|_{13} = -2 \sum_{J=2,4} (-1)^{J_0+k+F} \left\{ \begin{matrix} J_0 & k & F \\ k & J_0 & J \end{matrix} \right\} \langle k || C_J || k \rangle \left\langle \frac{1}{r^6} \right\rangle_k \times \\ \frac{[J]}{\sqrt{21}} \langle 3 || C_J || 1 \rangle \sum_{J_n} \left\{ \begin{matrix} 3 & J_0 & J_n \\ J_0 & 1 & J \end{matrix} \right\} \frac{\langle J_0 || \sum_i r_i^3 C_3 || J_n \rangle \langle J_n || \sum_j r_j C_1 || J_0 \rangle}{E_n - E_0}. \quad (26)$$

We note that

$$\langle 3 || C_2 || 1 \rangle = \frac{3\sqrt{5}}{5} \quad \text{and} \quad \langle 3 || C_4 || 1 \rangle = -\frac{2\sqrt{3}}{3},$$

and further that $\langle 1 || C_J || 3 \rangle = \langle 3 || C_J || 1 \rangle$, for $J = 2, 4$. This completes the second-order energy contributions that fall off as $1/r^6$.

3.1.3 Summary

The contributions to the second-order polarization energy that fall off as $1/r^4$ and $1/r^6$ are given by Eqs. (20), (24), (25), and (26), above. The contributions to the first-order energy fall off as $1/r^3$ and $1/r^5$. These first-order contributions are given given in Eq. (10).