Calculation of Effective Coulomb Interaction for $Pr^{3+}$, $U^{4+}$, and $UPt_3$

M.R. Norman

Materials Science Division, Argonne National Laboratory, Argonne, IL 60439
(June 28, 2021)

Abstract

In this paper, the Slater integrals for a screened Coulomb interaction of the the Yukawa form are calculated and by fitting the Thomas-Fermi wavevector, good agreement is obtained with experiment for the multiplet spectra of $Pr^{3+}$ and $U^{4+}$ ions. Moreover, a predicted multiplet spectrum for the heavy fermion superconductor $UPt_3$ is shown with a calculated Coulomb U of 1.6 eV. These effective Coulomb interactions, which are quite simple to calculate, should be useful inputs to further many-body calculations in correlated electron metals.

71.27.+a, 71.28.+d, 31.20.Tz, 32.30.-r

Typeset using REVTeX
Calculations of effective Coulomb interactions are important not only in atomic spectroscopy but also in condensed matter physics where the problem of correlated electron metals has received renewed attention with the discovery of heavy fermion and high temperature superconductivity. Even for an isolated atom, these calculations are difficult given the large number of possible configurations which must be considered and in the case of heavy ions, the added complication of taking into account relativistic effects. Only recently have detailed configuration interaction (CI) calculations been performed on $Pr^{3+}$, the prototype ion usually considered when trying to understand $f$ electron correlations. No similar calculations exist for $U^{4+}$, the actinide analogue of $Pr^{3+}$. The latter ion is of significance in condensed matter physics since uranium heavy fermion metals are lattices of such ions. In fact, recent studies of the $f^1$-$f^2$ Anderson lattice model show that atomic correlations can have a profound impact on the mean-field quasiparticle bands. Moreover, it has been proposed that such correlations also appear in the residual quasiparticle-quasiparticle interactions and are responsible for heavy fermion superconductivity. If anything, a proper understanding of these atomic correlations will be necessary to achieve a complete picture of heavy fermion physics since uranium heavy fermion metals are lattices of such ions. The standard method for interpreting multiplet spectra in heavy ions is to perform a least squares fit of the spectra using a Hamiltonian with adjustable coefficients. The main terms for $f^n$ spectra are the effective Slater integrals $F^L$ (L=0,2,4,6) and the spin-orbit splitting. Smaller terms corresponding to odd L due to configuration interaction plus other magnetic terms, which are necessary to get an exact fit to the spectra, are ignored here. These effective Slater integrals are considerably smaller than their Hartree-Fock values. This is as expected since the effect of correlations is to screen these values (in CI language, the $f$ electron is distributed in other configurations, thus reducing the wavefunction overlap and decreasing the value of these integrals). It is difficult, though, to calculate these effective integrals from first principles. Morrison and Rajnak have shown that the corrections from many-body perturbation theory have a slow convergence for $Pr^{3+}$. Recently, Cai et al have performed detailed configuration interaction calculations for $Pr^{3+}$ including up to 1708 configurations for each J state. The agreement with experiment is significantly improved over Hartree-Fock, but there are still some discrepancies.

Here, an approach intermediate between the fitting procedure and that of the ab initio calculations is taken. The reason for the problems mentioned above is that both ab initio methods are rather inefficient in calculating these effects. In solid state physics, one has to sum infinite series to describe screening effects properly, so the lack of convergence at third order in the above many-body perturbation calculation is not too surprising for an atom with a large number of electrons like $Pr$. As for CI, wavefunction expansions of this sort have very slow convergence except for small atoms when most of the correlation is coming from near degeneracy effects such as $Be$. Again, these problems are more severe when large numbers of electrons are involved. The most efficient way of dealing with this, then, is to
assume a screened interaction from the outset. In particular, in this paper, a Yukawa form
is used

\[ V(\vec{r}_1, \vec{r}_2) = e^{-\lambda|\vec{r}_1 - \vec{r}_2|} \left| \frac{\vec{r}_1 - \vec{r}_2}{|\vec{r}_1 - \vec{r}_2|} \right| \]  

(1)

The work of this paper is still semi-phenomenological in that \( \lambda \), the Thomas-Fermi wavevec-
tor, is treated as an adjustable constant. Ab initio calculations of it would suffer the same
slow convergence problems as mentioned above for the many-body perturbation calculation,
but at least our ignorance has been transferred to just one parameter as opposed to sev-
eral of them as in the least squares fitting to the experimental spectra discussed above. In
solids, reducing the fitting parameter to one number is highly desirable since the detailed
information available in atomic spectroscopy is often lost due to hybridization effects.

The Slater integrals of the Yukawa model are easily found. Just as the bare Coulomb
interaction is expandable in powers of \( r \), the screened interaction is expandable in spherical
functions

\[ V(\vec{r}_1, \vec{r}_2) = -\lambda \sum_L (2L + 1) j_L(i\lambda r_<)h_L^{(1)}(i\lambda r_>)P_L(\cos \theta) \]  

(2)

where \( j_L \) is a spherical Bessel function, \( h_L^{(1)} \) is a spherical Hankel function of the first kind,
and \( P_L \) is a Legendre polynomial, with \( \theta \) the angle between \( \vec{r}_1 \) and \( \vec{r}_2 \) and \( r_< \) (\( r_> \)) the
lesser (greater) of the two. These spherical functions were determined using routines in
Numerical Recipes. \[10\] The wavefunctions used in the Slater integrals were determined
from relativistic Hartree-Fock calculations. \[7\] For convenience, a single integral is defined
by taking a weighted contribution of the two spin-orbit wavefunctions, that is \( \phi_7^2 \in \) the
non-relativistic Slater integrals is replaced by \( \frac{3}{7}\phi_{5/2}^2 + \frac{4}{7}\phi_{7/2}^2 \).

In Fig. 1, the evolution of these Slater integrals versus \( \lambda \) for the \( U^{4+} \) case is shown (\( \lambda=0 \)
is the Hartree-Fock result). The \( L=0 \) integral is strongly screened whereas the higher \( L \)
integrals are less affected. This is to be expected since the former is a charge fluctuation
integral whereas the latter are shape fluctuation integrals. For all \( L \), the larger the \( L \), the
smaller the screening effect, as expected.

The matrix elements of the secular matrix for the \( f^2 \) ion case are listed by Goldschmidt.\[11\] There are 13 eigenvalues (3 triplets, 4 singlets, each of the triplets being split by
spin-orbit). The spin-orbit splitting determined from the relativistic Hartree-Fock orbitals
matches the experimental estimate \[8\] for \( Pr^{3+} \) to within 0.1%. This is as expected since
the spin-orbit interaction is a one-body force. Implications from the fits that this interaction
is screened was incorrect because non-relativistic estimates had been used for the Hartree-
Fock value. A slight discrepancy was found in the \( U^{4+} \) case in that the Hartree-Fock value
underestimated the experimental fit by about 2%. This is probably due to the strong in-
termediate coupling (LS versus jj) nature of the \( U \) ion. For the purposes of this paper, the
calculated Hartree-Fock values of \( \xi \) are used (where \( 7/2 \xi \) is equal to the splitting of the \( 5/2 \)
and \( 7/2 \) levels) as opposed to the ”experimental” ones. These values are 0.0990 eV for \( Pr^{3+} \)
and 0.2387 eV for \( U^{4+} \). The secular matrix is then diagonalized using Slater integrals for
a particular value of \( \lambda \). The energy of all levels will be refered to that of the ground state
\((^3H_4)\).
Results are shown for $Pr^{3+}$ in Fig. 2 with Slater integrals listed in Table 1. An RMS error of 82 meV is obtained for $\lambda = 2.0$. If the highest level ($^1S_0$) is ignored, an RMS error of 40 meV is obtained for $\lambda = 1.9$. This is to be compared to the RMS error of the CI calculation [1] which is 163 meV. An interesting point is that the ordering of the levels agrees with experiment, therefore questions raised [1] about the assignment of the $^1I_6$ level are probably not valid. Another point is that the values of the L=2 and L=4 Slater integrals agree with the fitted (experimental) values. On the other hand, the L=6 one is substantially larger. The quoted experimental value may be somewhat misleading, as it is more screened over Hartree-Fock than than the L=4 one, whereas one would conceptually expect that higher L integrals are less screened than lower L ones (as is indeed reproduced here). This leads to the possibility that there is another least squares fit to the data which more closely matches the current predictions. Such a fit would presumably have different values of the odd L interactions than listed in the published fits. This issue will be discussed in more detail in the next paragraph. Finally, the calculated L=0 Slater integral (the Coulomb repulsion, $U$) is close to the experimental estimates of 5.3 eV [12] and 5.5 eV [13]. This is quite interesting since the fit of $\lambda$ does not involve $U$. This suggests that the current method provides a trivial and independent way of estimating the Coulomb $U$. These estimates of $U$ are important inputs to many-body calculations in solids.

In Fig. 3 and Table 1, results are shown for $U^{4+}$. For $\lambda = 1.6$, an RMS error of 84 meV is obtained. If the highest level ($^1S_0$) is ignored, an RMS error of 40 meV is obtained for $\lambda = 1.5$. These deviations are identical to that found for $Pr^{3+}$, with $\lambda$ smaller in this case since the 5f orbitals are more delocalized than the 4f ones. The level ordering agrees with experiment except for an interchange of $^1D_2$ and $^1G_4$. The level ordering in this energy range (including $^3P_0$) is rather sensitive to $\lambda$, and this minor problem is almost certainly due to the intermediate coupling nature of this ion. This has been checked by directly replacing the Slater integral routines in the relativistic Hartree-Fock code by the Yukawa ones (there is a large number of Slater integrals due to the various combinations of the two spin-orbit radial functions). In this case, the ordering of the two levels comes out correct, but at the expense of having the $^3P_0$ lower than these two, as opposed to higher as in experiment. In fact, the RMS errors are larger with this approach; in particular, the splittings within an LS term are worse than with the other approach (these splittings have a weak dependence on $\lambda$). This again points to the intermediate coupling nature of the ion as the problem. Finally, as in $Pr^{3+}$, the predicted L=6 Slater integral is much less strongly screened than implied by the experimental least squares fits. [12] On the other hand, the value reported by Goldschmidt [11] is 0.3 eV larger than that quoted by Van Deurzen et al. [14] This difference is due to different definitions of the odd L interactions which in turn alters the values of the even L Slater integrals. [8] Inclusion of these odd L terms improves the RMS error of the current work by over a factor of 3, not surprising since 3 more fit parameters have been added. [13] First principles calculations of these odd L terms have had mixed success, [2] so their use is somewhat dangerous.

Also reported in Fig. 3 and Table 1 are results for $\lambda = 2.6$. This value was chosen to fit the $^3H_4 - ^3F_2$ splitting in $UPt_3$ observed with high energy neutron scattering. [16] This can then be taken as a prediction for the entire multiplet spectrum in this case. It should be remarked, though, that given the itinerancy of the f electrons in $UPt_3$, such multiplet effects will be very weak. They will probably be better observable in $UPd_3$, where the f electrons
are known to be localized and which has an almost identical observed splitting. Of more interest is the U value, which is necessary in many-body calculations. The predicted free ion value of 3.3 eV is larger than the experimental values quoted by Brewer [12] of 2.3 and 2.6 eV, although it should be remarked that these values were extracted from neutral ions with an $f^3$ ground state, and thus this U is expected to be smaller than the one appropriate for the more localized $U^{4+}$ ion. Also, U is predicted here to be reduced by a factor of two in the metallic environment appropriate for $UPt_3$ and $UPd_3$. This U value of 1.6 eV should be a useful input for many-body calculations in uranium heavy fermion metals. [17]

In conclusion, a simple method has been proposed for determining the effective Coulomb integrals needed for many-body calculations, including the Coulomb U. This method has been applied to $Pr^{3+}$ and $U^{4+}$ ions and gives reasonable values for these parameters. In turn, this method was used to give a prediction of such values for the case of uranium heavy fermion metals.

ACKNOWLEDGMENTS

This work was supported by the U.S. Dept. of Energy, Basic Energy Sciences, under Contract No. W-31-109-ENG-38. The author acknowledges Ray Osborn and Charlotte Froese Fischer for helpful discussions.
REFERENCES

[1] Z. Cai, V.M. Umar, and C.F. Fischer, Phys. Rev. Lett. 68, 297 (1992).
[2] J.C. Morrison and K. Rajnak, Phys. Rev. A 4, 536 (1971).
[3] P.A. Lee, T.M. Rice, J.W. Serene, L.J. Sham, and J.W. Wilkins, Comm. Cond. Mat. Phys. 12, 99 (1986).
[4] B.R. Trees, A.J. Fedro, and M.R. Norman, Phys. Rev. B 51, xxxx (1995).
[5] D. van der Marel and G. A. Sawatzky, Solid State Comm. 55, 937 (1985).
[6] M.R. Norman, Phys. Rev. Lett. 72, 2077 (1994); Phys. Rev. B 50, 6904 (1994).
[7] I.P. Grant et al, Comp. Phys. Comm. 21, 207 (1980).
[8] Z.P. Goldschmidt, in Handbook on the Physics and Chemistry of Rare Earths, Vol. 1, eds. K.A. Gschneidner, Jr. and L. Eyring (North Holland, Amsterdam, 1978), p. 1.
[9] F.W. Byron and R.W. Fuller, Mathematics of Classical and Quantum Physics, Vol. 2 (Addison-Wesley, Reading, 1970), p. 430.
[10] W.H. Press, B.P. Flannery, S.A. Teukolsky, and W.T. Vetterling, Numerical Recipes, 2nd Ed. (Cambridge Univ. Pr., Cambridge, 1992), Section 6.7.
[11] Z.B. Goldschmidt, Phys. Rev. A 27, 740 (1983).
[12] L. Brewer, J. Opt. Soc. Am. 61, 1101 (1971).
[13] J.K. Lang, Y. Baer, and P.A. Cox, J. Phys. F 11, 121 (1981).
[14] C.H.H. VanDeurzen, K. Rajnak, and J.G. Conway, J. Opt. Soc. Am. B 1, 45, (1984).
[15] This requires that $\lambda$ be reduced to 1.4 since the odd L terms are now accounting for some of the correlation. The fitted odd L terms are close to the reported values except for the $\beta$ term which is significantly differently (the $\beta$ term only affects $1S_0$).
[16] R. Osborn, K.A. McEwen, E.A. Goremychkin, A.D. Taylor, Physica B 163, 37 (1990).
[17] M.M. Steiner, M. Alouani, R.C. Albers, L.J. Sham, Physica B 199-200, 186 (1994).
TABLE I. Slater integrals (eV) for $Pr^{3+}$, $U^{4+}$, and $Up_{3}$. In column 2, HF is Hartree-Fock, exp is experiment, and the numbers refer to values of $\lambda$. The experimental estimates were taken from Ref. [12,13] ($Pr$, $L=0$), Ref. [8] ($Pr^{3+}$, $L>0$), Ref. [12] ($U$, $L=0$), and Ref. [14] ($U^{4+}$, $L>0$).

|        | $F^0$  | $F^2$  | $F^4$  | $F^6$  |
|--------|--------|--------|--------|--------|
| $Pr^{3+}$ | HF     | 25.722 | 12.227 | 7.670  | 5.517  |
|         | 1.9    | 5.560  | 9.000  | 6.811  | 5.190  |
|         | 2.0    | 5.230  | 8.784  | 6.735  | 5.158  |
|         | exp    | 5.355  | 9.090  | 6.927  | 4.756  |
| $U^{4+}$ | HF     | 18.796 | 9.482  | 6.202  | 4.552  |
|         | 1.6    | 3.309  | 6.377  | 5.281  | 4.185  |
|         | exp    | 2.326  | 6.440  | 5.296  | 3.441  |
| $Up_{3}$ | 2.6    | 1.645  | 4.421  | 4.336  | 3.724  |
FIGURES

FIG. 1. Slater integrals (eV) versus $\lambda$ (Thomas-Fermi wavevector in a.u.) for the $U^{4+}$ ion.

FIG. 2. Multiplet spectra (eV) relative to the $^3H_4$ ground state of $Pr^{3+}$ for Hartree-Fock (HF), $\lambda=2.0$ (2.0), experiment (exp) $\mathbb{I}$, and configuration-interaction (CI) $\mathbb{I}$. The first excited state is $^3H_5$.

FIG. 3. Multiplet spectra (eV) relative to the $^3H_4$ ground state of $U^{4+}$ for Hartree-Fock (HF), $\lambda=1.6$ (1.6), experiment (exp) $\mathbb{I}$, and $\lambda=2.6$ (2.6). The latter $\lambda$ was fit to the observed multiplet splitting in $UPt_3$. $\mathbb{I}$ The first excited state is $^3F_2$ except for Hartree-Fock where it is $^3H_5$. 
Energy (eV)

HF 1.6 exp 2.6