Ligand Field Theory Calculation of LuOH⁺

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Abstract

We have used a ligand field model proposed by Rice, Martin and Field (J. Chem. Phys. 82, 5023 (1985)) to describe the low-lying states of the lutetium monohydroxide cation. In this approach, the hydroxide anion is approximated as a polarizable negative charge. The molecular wave functions are expressed as linear combinations of the free-ion wave functions of Lu^{2+} that we obtained by using a model potential method developed by Klapisch. In preparation of calculating the electronic structure of lutetium monohydroxide, we performed benchmark calculations of three other molecules: CaF, LuO and CaOH.

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1 Introduction

The molecular ion LuOH⁺ is a promising candidate for precision measurements of fundamental CPsymmetry violation [1]. Such experiments would involve preparing the LuOH⁺ molecule in the 'science state', an excited vibrational state of the ${}^{2}\Sigma_{1/2}$ ground electronic state via transitions through the ${}^{2}\Pi_{1/2}$ state. However, there are no known recorded spectra of this molecule, and hence there is no available information about these transitions.

In order to get a first approximation of the electronic structure of LuOH⁺, we decided to use ligand field theory (LFT), or more precisely the ligand field approach proposed by Rice, Martin and Field (RMF) [2]. LFT is a simple alternative to much more demanding ab initio methods and its application has been quite successful. It has been shown that LFT can accurately predict electronic energies, transition moments, and other molecular constants of diatomic molecules such as alkaline earth monohalides [2, 3]. The electronic structure of alkaline earth monohalides MX with $M \in \{Ca, Sr, Ba\}$ and $X \in \{F, Cl, Br, I\}$ may be described as a single valence electron outside two closed-shell ions M^{2+} and X^{-} . The same can be done for LuOH⁺ where we have ions Lu³⁺ and OH⁻ instead. Within the ligand field model the ligand X⁻, or OH⁻ in our case, is approximated as a polarizable negative point charge that perturbs the one electron valence structure of the central ion. In this treatment, this means that the molecular Hamiltonian is the free-ion Hamiltonian where we add a point charge as a perturbation. The eigenvalues and eigenfunctions of the Hamiltonian are obtained using degenerate perturbation theory. As a consequence, the electronic states of the molecule are described as linear combinations of functions associated with the central free ion. Therefore, the ligand field calculation requires the knowledge of the free-ion energy levels and wave functions of Lu^{2+} and the equilibrium distance between the central ion Lu^{2+} and the ligand OH^{-} .

The energy levels and the equilibrium distance are quantities that have been measured or calculated and can be looked up. We computed the free-ion wave functions using a model potential approach developed by Klapisch which was also used by Allouche, Wannous and Aubert-Frécon (AWA) [3]. We tested it on Ca⁺ and then used it on Lu²⁺. After that we had the means to perform ligand field calculations for CaF, CaOH, LuO, LuOH⁺. In a first step, we tested our ligand field calculation on CaF and compared our results with the ones of RMF. Secondly, the LuO calculation was executed and compared with the measured LuO spectrum in the hope of learning something about the quality of our Lu²⁺ wave functions and the suitability of LFT for heavy atoms such as Lutetium. Since we treat the ligand by modelling it as a polarizable point charge, we calculated the spectrum of CaOH to test how well satisfied this approximation is for OH⁻. At the end we performed the ligand field calculation of Lutetium monohydroxide. We compared our calculated results with experimental energy levels, except for LuOH⁺ of course.

2 Ligand field calculation

In the following section we shall describe the ligand field calculation of RMF.

We divide a molecule MX into three interacting subsystems: two closed-shell ions M^{I+} and $X^{I'-}$ and the M^{I+} -centred valence electron e $(I, I' \in \mathbb{N})$. For now we will pretend that $X^{I'-}$ is a charged atom and not a charged molecule, like OH^- , which for LuOH⁺ it will eventually be. If we group under the name H^{core} all the terms that do not involve the valence electron¹, the nonrelativistic Hamiltonian that describes the total system is expressed, in atomic units, by

$$H = H^{\text{core}} - \frac{\Delta}{2} + \left(-\frac{Z_{\text{M}}}{r_{e\text{M}}} + \sum_{i \in \text{M}^{I+}} \frac{1}{r_{ei}} \right) + \left(-\frac{Z_{\text{X}}}{r_{e\text{X}}} + \sum_{i \in \text{X}^{I'-}} \frac{1}{r_{ei}} \right),\tag{1}$$

where $-\Delta/2$ is the kinetic energy of the valence electron, Δ is the Laplacian, the two terms in the parentheses are the electrostatic potential energies between the electron and the two ions. The summation goes over all electrons of the M^{I+} and X^{I'-} closed-shell ions. The variables $Z_{M,X}$ are the nuclear charges of M and X, r_{eM} and r_{eX} are the electron-core distances. In ligand field theory we replace the ligand X^{I'-} by a point charge with a charge equal to that of I' electrons, i.e., the term in

¹That would be the kinetic energies of the cores and their closed-shell electrons and the electrostatic potential energies between all combinations of the two cores and all involved closed-shell electrons.

the second parenthesis becomes I'/r_{eX} ,

$$H \approx H^{\text{core}} + \underbrace{\left(-\frac{\Delta}{2} - \frac{Z_{\text{M}}}{r_{e\text{M}}} + \sum_{i \in \text{M}^{I+}} \frac{1}{r_{ei}}\right)}_{H^{\text{M}}} + \frac{I'}{r_{e\text{X}}}.$$
(2)

Since we are interested in calculating energy differences only, the constant term H^{core} can be omitted. The term in parenthesis, which we shall name H^{M} , is the Hamiltonian of the valence electron in the M^{I+} ion potential. We can rewrite it using the free-ion energies E_{nl}^{M} of M^{I+} and its single-electron wave functions Ψ_{nlm} which satisfy

$$H^{\mathrm{M}} |\Psi_{nlm}\rangle = E_{nl}^{\mathrm{M}} |\Psi_{nlm}\rangle.$$
(3)

The electron-ligand interaction I'/r_{eX} shall henceforth be called H^{LF} . As a result, the terms of interest are

$$H^{\rm M} + H^{\rm LF} = \sum_{nlm} |\Psi_{nlm}\rangle E^{\rm M}_{nl} \langle \Psi_{nlm}| + \frac{I'}{r_{e\rm X}}.$$
(4)

We can use Laplace's expansion in order to express $H^{\rm LF}$ in spherical coordinates:

$$H^{\rm LF}(R_{\rm MX}) = \frac{I'}{r_{e\rm X}} = I' \sum_{k=0}^{\infty} \sqrt{\frac{4\pi}{2k+1}} Y_k^0(\theta,\phi) B_k(R_{\rm MX})$$
(5)

with

$$B_k(R_{\rm MX}) = \begin{cases} \frac{r^k}{R_{\rm MX}^{k+1}}, & r < R_{\rm MX} \end{cases}$$
(6)

$$\begin{cases}
\frac{R_{\rm MX}^k}{r^{k+1}}, & r > R_{\rm MX}
\end{cases}$$
(7)

where Y_l^m is a spherical harmonic function, $R_{\rm MX}$ is the equilibrium internuclear distance between M and X. The variable $r \equiv r_{e\rm M}$ is distance of the valence electron from the M^{I+} centre. The matrix $H^{\rm LF}$ in the basis of the free-ion wave functions $|\Psi_{nlm}\rangle$ is called the ligand field matrix. Because of the spherical symmetry of $H^{\rm M} + H^{\rm LF}$, we can write the free-ion wave functions in the following form

$$\Psi_{nlm}(r,\theta,\phi) = R_{nl}(r)Y_l^m(\theta,\phi),\tag{8}$$

then the ligand field matrix has matrix elements

$$H_{nlm,n'l'm'}^{\rm LF} = \langle \Psi_{nlm} | H^{\rm LF}(R_{\rm MX}) | \Psi_{n'l'm'} \rangle$$

$$= I' \sum_{k=0}^{\infty} \sqrt{\frac{4\pi}{2k+1}} (-1)^m \int Y_l^{-m}(\Omega) Y_k^0(\Omega) Y_{l'}^{m'}(\Omega) d\Omega \int_0^\infty R_{nl}(r) B_k(R_{\rm MX}) R_{n'l'}(r) r^2 dr.$$
(10)

 $d\Omega$ is the differential of the solid angle. Looking at this formula we can recognize the so-called Gaunt coefficients:

$$Y(l,k,l',-m,0,m') = \int Y_l^{-m}(\Omega) Y_k^0(\Omega) Y_{l'}^{m'}(\Omega) \, d\Omega$$
(11)

$$= \sqrt{\frac{(2l+1)(2k+1)(2l'+1)}{4\pi}} \begin{pmatrix} l & k & l' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l & k & l' \\ -m & 0 & m' \end{pmatrix}}.$$
 (12)

The two 2×3 matrices are Wigner 3j symbols. The Gaunt coefficients are zero unless m = m', $|l - l'| \le k \le l + l'$ and l + l' + k is an even integer. It follows that H^{LF} is a symmetric matrix and the infinite sum over k has a finite number of non-zero terms.

The eigenvalues of $H^{\rm M} + H^{\rm LF}$ are the ligand field energy levels. The eigenfunctions are linear combinations of the one-electron free-ion wave functions. In order to calculate them, we truncate the basis of the free-ion wave functions. RMF executed three different model calculations, namely C-3, C-7 and CP-7, where the numerals indicate of how many free-ion wave functions the basis consists. CP-7 includes the ligand polarization term H^{μ_-} , which will be explained in the remainder of this section.

The point charge approximation of the ligand can be improved by including the contribution of a dipole moment induced at the ligand by the field of the M^{I+} charge. The additional term to the ligand field part H^{LF} of the Hamiltonian is

$$H^{\mu_{-}}(R_{\rm MX}) = -\vec{E}(R_{\rm MX}) \cdot \vec{\mu}_{-}(R_{\rm MX}) = -\frac{\mu_{-}}{e} \frac{d}{dR} \left(H^{\rm LF}(R) \right) |_{R=R_{\rm MX}}$$
(13)

where $\vec{E}(R_{\rm MX})$ is the electric field at the X^{I'-} ion created by the valence electron and

$$\mu_{-} = \frac{\alpha_{-}}{R_{\rm MX}^2} \tag{14}$$

is the point dipole moment. The quantity α_{-} is the ligand polarizability which is an input to the theory for a given ligand X, and must either be experimentally determined or calculated.

This model is free of adjustable parameters and relies only on experimental free-ion M^{I+} energy levels, single-electron wave functions and the measured equilibrium bond lengths R_{MX} of the MX molecules. If we include $H^{\mu-}$ in the Hamiltonian, then also on α_{-} .

3 Calculation of wave functions

One necessity for a ligand field calculation are high-quality free-ion wave functions. Since we are interested in C-7 and CP-7 calculations we needed to find the seven wave functions corresponding to the seven states lowest in energy.

3.1 Klapisch model potential

In their paper [3], AWA used basis functions built from a Klapisch-type model potential describing the interaction of the valence electron with the closed-shell core M^{2+} (M \in {Ca,Sr,Ba}).

In his PhD thesis [10], Klapisch developed this method for calculating wave functions, which we shall briefly outline. In the non-relativistic regime and neglecting spin-orbit interaction, the Hamiltonian of an atom with N electrons is

$$H = \sum_{i=1}^{N} \left(-\frac{\Delta_i}{2} - \frac{Z}{r_i} \right) + \sum_{i>j} \frac{1}{r_{ij}}.$$
 (15)

Z is the nuclear charge. Because the electron-electron interaction terms $1/r_{ij}$ prevent separation of variables, it is impossible to find exact solutions. Instead, the common approach is to introduce a central potential $V(r_i)$ that represents the average potential in which each electron resides:

$$H = \underbrace{\sum_{i=1}^{N} \left(-\frac{\Delta_i}{2} + V(r_i) \right)}_{H_0} + \sum_{i=1}^{N} \left(-V(r_i) - \frac{Z}{r_i} \right) + \sum_{i>j} \frac{1}{r_{ij}}.$$
 (16)

We can easily obtain the solutions of H_0 because the variables of the different electrons are now separable. We have

$$H_0 \Psi = E^{(0)} \Psi \tag{17}$$

$$\left(\sum_{i} h_{i}\right) \left(\prod_{i} \Psi_{i}\right) = \left(\sum_{i} \epsilon_{i}\right) \left(\prod_{i} \Psi_{i}\right)$$
(18)

with

$$h_i = -\frac{\Delta_i}{2} + V(r_i), \tag{19}$$

$$h_i \Psi_i = \epsilon_i \Psi_i \tag{20}$$

for i = 1, ..., N. As in the ligand field calculation, we can make use of the spherical symmetry of $V(r_i)$ and then identify the angular function as the spherical harmonic function.

$$\Psi_i \equiv \Psi(r_i, \theta_i, \phi_i) = R(r_i)Y(\theta_i, \phi_i) \qquad \Rightarrow \qquad \Psi_{nlm}(i) = \frac{u_{nl}(r_i)}{r_i}Y_l^m(\theta_i, \phi_i) \tag{21}$$

If we start from equation (20), using the form of the wave function in equation (21), the definition of the Laplacian Δ in spherical coordinates and the eigenvalue equation of the spherical harmonics functions, we obtain the radial one-electron Schrödinger equation:

$$\left(-\frac{1}{2}\frac{\partial^2}{\partial r_i^2} + \frac{1}{2r_i^2}l(l+1) + V(r_i)\right)u_{nl}(r_i) = \epsilon_{nl}u_{nl}(r_i),\tag{22}$$

with

$$u_{nl}(r_i) = r_i R_{nl}(r_i), (23)$$

which we can solve and therefore find all single-electron energies ϵ_i and single-electron wave functions Ψ_i . This allows us to calculate the total energy $E^{(0)}$ and the total wave function Ψ of the unperturbed Hamiltonian H_0 . Therefore this trick of introducing a central potential enables us to apply perturbation theory to complex atoms and calculate the energies and wave functions of the full Hamiltonian H.

If the calculations are exact, the choice of $V(r_i)$ does not matter. Klapisch formulated different criteria for determining the quality of a potential $V(r_i)$. These criteria entail minimising a functional which proves to be a very difficult task. Therefore Klapisch realised that finding the optimal potential in all generality is impossible and one must impose restrictions on the class of functions $V(r_i)$. The first restriction is:

$$V_j(r_i) = U(r), \qquad i = 1, \dots, N$$
 (24)

$$j = 0, \dots, \infty \tag{25}$$

which means that for a state j of the considered atom, all the mono-electronic functions Ψ_i are solutions of the same Hamiltonian and are therefore orthogonal. This not only simplifies but is in fact a necessity for the use of perturbation theory.

The second restriction is much more important because it effectively allows us to find the minimum of the aforementioned functionals. We describe the potential $V(r_i)$ with an analytical function that depends on an ensemble of parameters $\underline{\alpha} = (\alpha_1, \ldots, \alpha_n)$.

$$V(r_i) = U(\underline{\alpha}, r), \qquad i = 1, \dots, N$$
(26)

The criteria of the quality of a potential are now associated with functions and not functionals anymore. The criterion we will use is what Klapisch calls the spectroscopic criterion where the parameters $\underline{\alpha}$ are adjusted to reproduce the known energy spectrum of the atom. The function we want to minimise is root-mean-square error

$$S_p(\underline{\alpha}) = \left[\sum_{j=1}^M \frac{1}{M} (E_j^{(p)}(\underline{\alpha}) - E_j^{\exp})^2\right]^{1/2}$$
(27)

for M energies chosen in advance, where p is the order of perturbation. If we choose to represent the potential as

$$V(r) = -\frac{Z_{\text{eff}}(r)}{r},\tag{28}$$

then we must have that

$$Z_{\text{eff}}(\infty) = Z - (N - 1) = I, \qquad Z_{\text{eff}}(0) = Z,$$
(29)

where N is the number of electrons. These conditions mean that the effective charges a single electron interacts with are I and Z for the electron being very far away from the core and very close to the core. A simple one-parameter potential that satisfies these conditions is

$$U(\alpha, r) = -\frac{I + (Z - I)e^{-\alpha r}}{r}.$$
(30)

Klapisch also came up with a 3-parameter model that had the following form:

$$U(\underline{\alpha}, r) = -\frac{I + (Z - I)e^{-\alpha_1 r} + \alpha_2 r e^{-\alpha_3 r}}{r}.$$
(31)

One problem of this potential is that the parameters have no physical meaning. That is why an estimate of an initial value for minimisation is difficult. Klapisch developed a more general formula which solves this problem. He calls it the complete formula.

$$U(\underline{\alpha}, r) = -\frac{I + \sum_{k=1}^{M} q_k g_{L_k}(\alpha_k, r) + \sum_{k'=1}^{M'} q_{k'} f_{l_{k'}}(\alpha_{k'}, r)}{r}$$
(32)

 $g_{L_k}(\alpha_k, r)$ describe the effect of the k-th complete shell with orbital quantum number L_k . The q_k and $q_{k'}$ are the number of electrons on each shell and subshell.

$$f_l(\alpha, r) = e^{-\alpha r} \sum_{j=0}^{2l+1} \left(1 - \frac{j}{2l+2} \right) \frac{(\alpha r)^j}{j!}$$
(33)

$$g_L(\alpha, r) = \frac{\sum_{l=0}^{L} (4l+2) f_l(\alpha, r)}{\sum_{l=0}^{L} (4l+2)}$$
(34)

Now how exactly did we use this to get our own wave functions? In our case, we forewent the use of perturbation theory, i.e p = 0, and derived a set of one-electron wave functions simply by solving the following equation:

$$h(\mathbf{M}^{(I-1)+})\Psi_{nlm} = \epsilon_{nl}\Psi_{nlm} \tag{35}$$

with

$$h(\mathbf{M}^{(I-1)+}) = -\frac{1}{2}\Delta + \sum_{l'} U_{l'}(r)P_{l'}$$
(36)

Exactly as AWA, we settled for the following 4-parameter potential $U_l(r)$ which is *l*-dependent. It consists of the 3-parameter potential (screening term) we have already seen and an additional polarization term:

$$U_l(r) = -\frac{1}{r} \left(I + (Z - I) \cdot e^{-\alpha_1^l r} + \alpha_2^l r e^{-\alpha_3^l r} \right) - \frac{\alpha_d}{2r^4} \left(1 - e^{-(r/r_c^l)^6} \right), \tag{37}$$

where r is the distance between the valence electron and the core M^{I+} , α_d is the dipole polarizability of the M^{I+} ion. P_l is a projection operator: $P_{l'}\Psi_{nlm} = \delta_{l',l}\Psi_{nlm}$. The parameters $\underline{\alpha} = (\alpha_1, \alpha_2, \alpha_3, r_c)$ vary for different l. This model potential has been used in other papers for alkaline-earth metals [7, 8] and for example Francium [9]. Again, we can reduce the 3-dimensional problem that is equation (35) to a one-dimensional problem:

$$-\frac{1}{2}\frac{\partial^2 u_{nl}}{\partial r^2} + \underbrace{\left(\frac{1}{2r^2}l(l+1) + U_l(r)\right)}_{U_l^{\text{eff}}(r)} u_{nl} = \epsilon_{nl}u_{nl},\tag{38}$$

where

$$\Psi_{nlm}(r,\theta,\phi) = \frac{u_{nl}(r)}{r} Y_l^m(\theta,\phi)$$
(39)

is the complete one-electron wave function. So the main task was to find parameters $\alpha_1, \alpha_2, \alpha_3$ and r_c that minimise the function

$$S^{l}(\underline{\alpha}) = \left[\sum_{j=1}^{M} \frac{1}{M} (\epsilon_{jl}(\underline{\alpha}) - E_{j}^{\exp})^{2}\right]^{1/2}$$
(40)

for l being 0, 1, 2, 3 and M chosen energy levels. Of course you want to consider as many energy levels as are available. Essentially we had to deal with a continuous optimisation problem in four variables.

3.2 Solving the Schrödinger equation

Part of the minimisation was solving equation (38) over and over again for different values of $\underline{\alpha} = (\alpha_1, \alpha_2, \alpha_3, r_c)$. We did this as follows: we discretize the radial coordinate in an equidistant grid of N elements.

$$[r_1, \dots, r_N] = \left[\frac{r_{\max}}{N}, 2\frac{r_{\max}}{N}, \dots, (N-1)\frac{r_{\max}}{N}, r_{\max}\right], \qquad r_{i+1} - r_i = h$$
(41)

This allows us to approximate the second derivative with finite differences:

$$f''(x_i) \approx \frac{f(x_{i-1}) - 2f(x_i) + f(x_{i+1})}{h^2}$$
(42)

As a consequence equation (38) turns into a system of equations:

$$\frac{u_{nl}(r_{i-1}) - 2u_{nl}(r_i) + u_{nl}(r_{i+1})}{2h^2} + U_l^{\text{eff}}(r_i)u_{nl}(r_i) = \epsilon_{nl}u_{nl}(r_i), \qquad i = 1, \dots, N$$
(43)

that can be regarded as a matrix eigenvalue equation. So essentially we have to find the eigenvalues and eigenvectors of the following matrix:

Obviously, valid wave functions must satisfy

$$u_{nl}(0) = u_{nl}(\infty) = 0, (45)$$

so we can set $u_{nl}(r_0 = 0) = 0$. At the end we have N + 1 function values for each eigenfunction which can be used for interpolation or we can try to find suitable fitting functions.

3.3 Ca⁺ wave functions

First we wanted to test the Klapisch model potential method on Ca⁺ and see if we could produce good Ca⁺ wave functions, namely 4s, 5s, 4p, 5p, 3d, 4d and 4f. AWA did not actually solve the optimisation problem themselves, they used the coefficients found by Aymar and Greene [7, 8]. The coefficients for Ca⁺ can been seen in table 1. Ultimately, we wanted to find out if we could reproduce these results. In this particular case, we had to set the nuclear charge Z = 20, I = 2 and the dipole polarizability of the Ca²⁺ ion $\alpha_d = 3.5 \cdot 4\pi\epsilon_0 a_0^3$ [7], ϵ_0 is the vacuum permittivity, a_0 is the Bohr radius. We used the 25 lowest Ca⁺-energy levels with l = 0, 1, 2, 3 from NIST [14]. Furthermore, we used a grid of N = 2250 points and set $r_{\text{max}} = 90 a_0$ to solve the Schrödinger equation.

The coefficients we calculated can be found in table 2. The largest difference between measured and calculated energy values for l = 0, 1, 2, 3 are 3.51, 0.59, 153, 127 cm⁻¹. One quickly notices that our coefficients are not identical to those of table 1, even though we chose initial values for the minimisation that were fairly close to the final values of Aymar. The resulting wave functions can be seen in figure 1, where one can compare them to the functions RMF used. They used the analytical 4s, 4p and 3d radial wave functions reported by Weiss [6]. The 5s, 5p, 4d and 4f functions were generated in a way explained in the appendix of RMF's paper. Our wave functions look a little bit different than the ones of RMF. 4s, 4p and 3d are very similar, the 5s functions still look very much alike. The others show significant differences. Especially the small peak of 5f for small r, see figure 1d, is a little bit worrying. This behaviour does not seem to be very physical. Nevertheless the results of the ligand field calculation for CaF which we obtained with these functions looked very promising, see section 4.1. Because of that we concluded that it might be worth a try to search for Lu²⁺ wave functions using the Klapisch model potential method, hoping that the subsequent ligand field calculations yield similarly good results.

\mathbf{Ca}^+	l	$\alpha_1 \left[1/a_0 \right]$	$\alpha_2 \left[1/a_0 \right]$	$\alpha_3 \left[1/a_0\right]$	$r_c \ [a_0]$
	0	4.0099	13.023	2.1315	1.6352
$\alpha_d = 3.5 a_0^3 [7]$	1	4.2056	12.658	2.0186	1.5177
	2	3.5058	12.399	2.2648	1.6187
	3	3.7741	13.232	3.1848	0.7150

Table 1: Empirical parameters of the model potential for Ca^+ calculated by Aymar and Telmini [7]. The constant a_0 is the Bohr radius.

Ca^+	l	$\alpha_1 \ [1/a_0]$	$\alpha_2 \left[1/a_0 \right]$	$\alpha_3 \left[1/a_0\right]$	$r_c [a_0]$
	0	3.7744	13.033	2.1497	1.5831
$\alpha_d = 3.5 a_0^3 \ [7]$	1	4.2699	12.590	2.0254	1.4901
	2	3.5226	12.388	2.2206	1.7592
	3	8.3048	12.714	9.1651	0.3738

Table 2: Empirical parameters of the model potential for Ca^+ obtained by solving optimisation problem. The constant a_0 is the Bohr radius.



(a) 4s, 4p and 3d wave functions used by RMF and found by Weiss [6].



(c) 5s, 5p, 4d and 4f wave functions used by RMF.



(b) 4s, 4p and 3d wave functions found by solving optimisation problem.



(d) 5s, 5p, 4d and 4f wave functions found by solving optimisation problem.

Figure 1: Comparison of the Ca^+ wave functions used by RMF (left figures) and our own wave functions (right figures).

3.4 Lu²⁺ wave functions

The goal was to find the seven wave functions corresponding to the lowest energies, i.e. 6s, 7s, 6p, 7p, 5d, 6d and 5f.

For Lu^{2+} , we set the nuclear charge Z = 71, I = 3 and the dipole polarizability of the Lu^{3+} ion $\alpha_d = 4.022 \cdot 4\pi\epsilon_0 a_0^3$ [11]. As before, the Lu^{2+} -energies were taken from NIST [14]. This time we used all 15 energy levels that were available for Lu^{2+} . The solving of the Schrödinger equation was executed with N = 8000 grid points and $r_{\max} = 90 a_0$.

The coefficients we found can be seen in table 3. One might notice that for l = 3 the coefficients seem to be off considering that the values for the other l are all fairly close together. What also stands out is that for l = 1, 2, the function $S(\underline{\alpha})$ is considerably smaller than for the other two l. This might have something to do with the number of available energy levels for each l. While for l = 1, 2 we had only two and three energy levels at our disposal, for l = 0, 3 we had five each. The largest difference between measured and calculated energy values for l = 0, 1, 2, 3 are $5.62, 7.7 \cdot 10^{-3}, 2.8 \cdot 10^{-4}, 163 \text{ cm}^{-1}$. It took quite the effort finding these values and with that the wave functions we used in the ligand field calculations. As already mentioned, it is not clear what initial values one should use. So what frequently happened was that, when looking for a function u_{nl} , we would obtain a function $u_{n'l}$. For example when searching for a 6s function we would find a 7s function. One can confirm this by counting nodes because the number of nodes of u_{nl} must be equal to n - l - 1.

For Ca⁺ we did not have this problem. Since we knew what we were looking for, i.e. the values of Aymar, we could simply choose initial values close to them. In the case of Lu²⁺, we spent a considerable amount of time trying the minimisation with different initial values. For each l we found many different sets of values, some of which correspond to a local minimum of $S(\underline{\alpha})$. Of course we do not know whether we found the global minimum.

For l = 0, 1, 2, the values of $\underline{\alpha} = (\alpha_1, \alpha_2, \alpha_3, r_c)$ in table 3 are the ones with the lowest value of $S(\underline{\alpha})$ we could make out. For l = 3 we found values of $\underline{\alpha}$ for which $S(\underline{\alpha})$ was smaller than $5.8264 \cdot 10^{-4} E_h$ (see table 3), the smallest was $4.2807 \cdot 10^{-4} E_h$. That is not a large difference but the question remains: why did we settle for the worse values?

While the global maximum of these different 5f wave functions was always at the same location with the same magnitude, we came across some significant differences between the different wave functions for small r. In the end we let the ligand field calculation of LuO decide, i.e. we chose the 5f function whose ligand field calculation yielded the best energy levels for LuO. Our final wave functions can be seen in figure 2.

Lu^{2+}	l	$\alpha_1 \left[1/a_0 \right]$	$\alpha_2 \left[1/a_0 \right]$	$\alpha_3 \ [1/a_0]$	$r_c \ [a_0]$	$S(\underline{\alpha}) \ [E_h]$
	0	3.9516	10.597	2.0542	1.4757	$1.4637 \cdot 10^{-5}$
$\alpha_d = 4.022 \ a_0^3 \ [11]$	1	4.2965	12.931	2.1446	1.4093	$3.8671 \cdot 10^{-8}$
	2	4.1696	10.067	1.9920	1.7785	$8.5418 \cdot 10^{-10}$
	3	3.6618	-3.5589	5.1305	1.6709	$5.8264 \cdot 10^{-4}$

Table 3: Empirical parameters of the model potential for Lu^{2+} obtained by solving optimisation problem. The constants a_0 and $E_h = \hbar^2/(m_e a_0^2) \approx 27.2 \text{ eV}$ are the Bohr radius and the Hartree energy.



Figure 2: Our own Lu^{2+} wave functions found by solving optimisation problem.

4 Results of ligand field calculations

4.1 CaF

The first step was to reproduce the results of RMF in order to test the ligand field calculation. If we use the notation introduced in section 2, then we have $M^{I+} = Ca^{2+}$ and $X^{I'-} = F^-$, i.e. the ligand has a charge of -e, that is why one has to set I' = 1 in the ligand field calculation. We used the same seven functions as RMF for our own C-7 and CP-7 calculations. Following that we did the same calculation with our own model potential wave functions. For CP-7 RMF approximated the ligand polarizability α_- as Pauling's ion polarizability [12], which in the case of CaF is 7.086 $\cdot 4\pi\epsilon_0 a_0^3$, and so did we. In [13] the authors of said paper talk about how this value is much too low compared to the recent theoretical value of $17.613 \cdot 4\pi\epsilon_0 a_0^3$. All energies were calculated at the equilibrium internuclear distance of the ground state X ${}^2\Sigma^+$. Our results are summarised in table 4.

As one can see, our energies are convincingly close to the ones of RMF. For C-7 the difference between our results are smaller than 88 cm^{-1} and for CP-7 smaller than 219 cm^{-1} . Why are they not identical? Most likely RMF used slightly different values for R_{CaF} and/or for the free-ion energy levels of Ca⁺. Unfortunately we do not know the exact values they used.

The energies obtained with our model potential wave functions are reasonably close to the ones of RMF. What is interesting is that for the first excited state our energy is worse than the one of RMF but for the other states our energies are better. The energy difference is only 812 cm^{-1} for the state B' $^{2}\Delta$. Overall we are quite content with these values. They convinced us that, using Klapisch's method, we might be able to find wave functions of decent quality for Lu²⁺ which we can use for a ligand field calculation of LuOH⁺.

Inspired by RMF's paper, we added figure 3 which nicely visualises the effects of the different terms in the C-7 calculation. The leftmost column starts with the free Ca⁺-ion energy levels. In the second column, these are shifted by the diagonal H^{LF} terms where we only include the k = 0 terms (see equation 10). We omit the overall upward shift of all orbital energies by 53453 cm⁻¹ and only show the shifts relative to the 4s orbital energy. Next, we include the full diagonal H^{LF} terms which partially lift the degeneracy of the free-ion levels. In the fourth column, the off-diagonal terms of H^{LF} are added, which mixes 4s, 4p and 3d and gives us the C-3 energy levels. In right most columns we expand the basis and go from the C-3 to the C-7 calculation, i.e. we allow configurational mixing with the 5s, 5p, 4d and 4f orbitals. RMF call these four additional orbitals Rydberg orbitals.

CaF $(R_{\text{CaF}} = 1.967 \text{ Å} [15])$	A $^{2}\Pi$	B $^{2}\Sigma^{+}$	B' $^{2}\Delta$	C $^{2}\Pi$
Measured [15]	16526	18845	21531	30270
RMF - C-7 [2]	17978	21463	-	32644
RMF - CP-7 [2] ($\alpha_{-} = 7.086 a_0^3$ [12])	17998	22376	-	32686
C-7	18018	21387	22786	32731
CP-7 ($\alpha_{-} = 7.086 a_0^3 [12]$)	18054	22332	24877	32904
C-7 - $N = 2250, r_{\text{max}} = 90 a_0$	18221	21379	22343	31896

Table 4: Experimental and calculated values for the energies of the four lowest excited states of CaF. The calculations C-7 and CP-7 use the same wave functions as RMF, the calculation in the last row uses our own wave functions. The capital letters A, B, C refer to the first, second and third excited state. Historically, the state B' was found after the state C had already been named, i.e. the state C is actually the fourth excited state. All energies are in cm^{-1} .



Figure 3: CaF: Effects of the different terms in the C-7 calculation (using the RMF wave functions) shown relative to the energies of the first three free Ca⁺-ion states. The overall upward shift of all orbital energies by 53453 cm^{-1} has been omitted.

4.2 LuO

The motivation for this calculation was to get an idea of the quality of our Lu²⁺ wave functions. Now we have $M^{I+} = Lu^{3+}$ and $X^{I'-} = O^{2-}$, that is why one has to set I' = 2 in the ligand field calculation. All energies were calculated at the equilibrium internuclear distance of the ground state X ${}^{2}\Sigma^{+}$. Our results are summarised in table 5.

While for the first excited state of CaF we had differences between the measured and calculated energies of about $1450 - 1700 \text{ cm}^{-1}$, the difference here is 2347 cm^{-1} . As it turns out our calculation shows that there should be an additional energy level which has not been measured. The difference in energy for the state C $^{2}\Sigma^{+}$ is 3282 cm^{-1} . Unfortunately we only have these two values for comparison. In this case we have larger differences than for CaF. One of the reasons for that is most likely because the quality of our wave functions for Lu²⁺ is not as good as for Ca⁺. However, overall our calculated energies are still quite satisfying.

As for CaF, we created an energy diagram, see figure 4. The leftmost energy levels are of the free Lu^{2+} -ion. From left to right we add more terms to the calculation: the k = 0 diagonal H^{LF} terms, next the $k \neq 0$ diagonal H^{LF} terms and then the off-diagonal H^{LF} terms. In the last column we expand the basis to seven basis functions.

LuO $(R_{\text{LuO}} = 1.7904 \text{ Å} [16])$	A $^{2}\Pi$	B $^{2}\Delta$	C $^{2}\Sigma^{+}$
Measured [16]	20777	_	24440
C-7 - $N = 8000, r_{\text{max}} = 90 a_0$	23124	25091	27722

Table 5: Experimental and calculated values for the energies of the three lowest excited states of LuO. The capital letters A, B, C refer to the first, second and third excited state. All energies are in cm⁻¹.



Figure 4: LuO: Effects of the different terms in the C-7 calculation shown relative to the energies of the first three free Lu^{2+} -ion states. The overall upward shift of all orbital energies by 121972 cm⁻¹ has been omitted.

4.3 CaOH

Because eventually we had to deal with a OH⁻ ligand in the calculation of LuOH⁺, we thought it might be interesting to see what kind of results we get for a molecule with the same ligand.

In this third ligand field calculation we have $M^{I+} = Ca^{2+}$ and $X^{I'-} = OH^-$. We reused the RMF Ca⁺ wave functions. Compared to the CaF calculation, we simply needed to adjust the internuclear distance R_{CaOH} and the polarizability of the ligand. But what exactly is R_{CaOH} ? CaOH is a triatomic molecule. Up to now, $X^{I'-}$ was a charged atom, now it is a charged diatomic molecule, i.e. it has two cores itself. Because oxygen is extremely electronegative, we can basically think of OH⁻ as an oxygen ion of charge -e with a neutral hydrogen atom attached to it. Therefore we decided to set $R_{CaOH} = R_{CaO}$ where R_{CaO} is the Ca-O bond length in the CaOH molecule when it is in the ground state, which is 1.976 Å [17].

Because R_{CaOH} is almost identical to the value of R_{CaF} , the energies of C-7 are very close to those of CaF, see table 6. In general one would expect that the results are not as good as the ones for CaF since the point charge approximation is more suitable for a fluoride ion than for the hydroxide anion. For the states A ²II and B ² Σ^+ this is indeed the case but for the third excited state we have a difference of only 818 cm⁻¹ to the measured value which is a remarkably good value. CaF had a difference of 1255 cm⁻¹. It is no surprise that the energy diagram for CaOH also looks practically identical to the one of CaF, see figure 5. Compared to CaF, the energies are shifted by 100 cm⁻¹ at the most.

In this paper [13], its authors discuss why the free-ion polarizability of OH^- , $\alpha_- = 26.791 \cdot 4\pi\epsilon_0 a_0^3$, which is known from ab initio calculations, is much too high to be used for a ligand field calculation of CaOH. Instead one can get better results by using a 'effective' polarizability of $9.11 \cdot 4\pi\epsilon_0 a_0^3$, which can be obtained by adjusting the polarizabilities of Ca⁺ and OH⁻ such that they reproduce the total dipole moment of CaOH. For more details, see [13]. That is why we decided to perform CP-7 calculations with both polarizabilities.

In conclusion, this calculation justifies the use of ligand field theory on molecules with a hydroxide ligand.

CaOH $(R_{CaOH} = 1.976 \text{ Å} [17])$	A $^{2}\Pi$	B $^{2}\Sigma^{+}$	C $^{2}\Delta$
Measured [18]	15998	18022	21896
C-7	18012	21347	22714
CP-7 ($\alpha_{-} = 26.791 a_0^3 [13]$)	17459	22271	28342
CP-7 ($\alpha_{-} = 9.11 a_0^3 [13]$)	18033	22480	25339

Table 6: Experimental and calculated values for the energies of the three lowest excited states of CaOH. The capital letters A, B, C refer to the first, second and third excited state. All energies are in $\rm cm^{-1}$.



Figure 5: CaOH: Effects of the different terms in the C-7 calculation shown relative to the energies of the first three free Ca⁺-ion states. The overall upward shift of all orbital energies by 53307 cm^{-1} has been omitted.

4.4 $LuOH^+$

For this final calculation we have $M^{I+} = Lu^{3+}$ and $X^{I'-} = OH^-$. Analogous to CaOH, we set the internuclear distance $R_{LuOH^+} = R_{LuO}$ where $R_{LuO} = 1.873$ Å is the Lu-O bond length in LuOH⁺ when it is in the ground state. For reasons discussed in the previous section, we knew that the polarizability of OH⁻, $\alpha_- = 26.791 \cdot 4\pi\epsilon_0 a_0^3$, would not yield good results. Unfortunately we did not have the means to calculate the 'effective' polarizability which is why we did three additional CP-7 calculations with lower polarizabilities in order to compare the effect it has on the energies. The results are summarised in table 7 and figure 6. Figure 7 shows the matching energy diagram.

LuOH ⁺ ($R_{LuOH^+} = 1.873$ Å [1])	A $^{2}\Pi$	B $^{2}\Sigma^{+}$	C $^{2}\Delta$
C-7 - $N = 8000, r_{\text{max}} = 90 a_0$	12925	16906	19520
CP-7 ($\alpha_{-} = 26.791 a_0^3 [13]$)	21146	24333	28235
CP-7 ($\alpha_{-} = 20.245 a_0^3$)	19148	23243	26886
CP-7 ($\alpha_{-} = 13.497 a_0^3$)	17059	21629	25049
CP-7 ($\alpha_{-} = 6.748 a_0^3$)	14974	19500	22635

Table 7: Calculated values for the energies of the three lowest excited states of $LuOH^+$ using the same Lu^{2+} wave functions as for LuO. The capital letters A, B, C refer to the first, second and third excited state. All energies are in cm⁻¹.



Figure 6: LuOH⁺: Visualisation of the results in table 7.

The wave functions obtained in the C-7 calculations are presented in tables 8 and 9. They are expressed in terms of the percentage composition of the single basis functions.



Figure 7: LuOH⁺: Effects of the different terms in the C-7 calculation shown relative to the energies of the first three free Lu^{2+} -ion states. The overall upward shift of all orbital energies by 59051 cm⁻¹ has been omitted.

		4s	4p	3d	Rydberg
CaF	X $^{2}\Sigma^{+}$	79	19	0	2
	A $^{2}\Pi$	0	63	32	5
	B $^{2}\Sigma^{+}$	7	33	53	7
	$\mathrm{B}^{\prime 2}\Delta$	0	0	96	4
	C $^{2}\Pi$	0	19	48	33
CaOH	${\rm X} {}^{2}\Sigma^{+}$	79	19	0	2
	A $^{2}\Pi$	0	63	32	5
	B $^{2}\Sigma^{+}$	7	33	53	7
	C $^{2}\Delta$	0	0	96	4

Table 8: Wave functions: Orbital mixing percentages for the C-7 calculations. Rydberg refers to the orbitals 5s, 5p, 4d and 4f.

.=		6s	6p	5d	Rydberg
LuO	X $^{2}\Sigma^{+}$	73	24	0	3
	A $^{2}\Pi$	0	40	47	13
	B $^{2}\Delta$	0	0	92	8
	C $^{2}\Sigma^{+}$	7	17	57	19
LuOH ⁺	${\rm X} {}^{2}\Sigma^{+}$	88	9	2	1
	A $^{2}\Delta$	0	0	99	1
	${\rm B}~^{2}\Pi$	0	10	88	2
	C $^{2}\Sigma^{+}$	0	18	79	3

Table 9: Wave functions: Orbital mixing percentages for the C-7 calculations. Rydberg refers to the orbitals 7s, 7p, 6d and 5f.

5 Discussion

We have successfully computed the ligand field energies of the lowest-lying states of CaF and LuO and CaOH and LuOH⁺. The accuracy could of course be better but given the simplicity of the model they are surprisingly satisfying. One should keep in mind that we have two kinds of shortcomings in our calculation. First the approximations of LFT will give us errors even if we used virtually perfect wave functions. However, since we do not know the free-ion wave functions perfectly, therein lies our second shortcoming.

We notice that for CaF, LuO and CaOH the ligand field energy levels are all consistently too large in comparison to the measured energies. We have no reason to believe that this is any different for LuOH⁺. We can make use of that fact and try to estimate the actual energy levels of LuOH⁺. Our calculated value of the energy of the A ²II state of LuO is 2347 cm⁻¹ too high. Going from CaF to CaOH the difference between calculated and measured energy for the first excited state increases about 35%. If we translate this to going from LuO to LuOH⁺, then our ligand field energy should be about 3168 cm⁻¹ too high. If we add an error of 1000 cm⁻¹, we get that the actual energy level of A ²II for LuOH⁺ lies in the range 8757 – 10757 cm⁻¹. This implies that the wavelength of the A-X transition lies between 1.14 and 0.93 μ m.

Another point, which RMF already noticed, is that the results for C-7 appear to agree better with experiment than those of CP-7. So it seems that this calculation is worthless for our use. RMF admit that the crude way the ligand polarizability is treated may be insufficiently accurate to improve on the simple point charge model. They say that the most important neglected polarization effect and the most difficult to include in the present calculation is the saturation of the ligand induced dipole moment μ_{-} . Nevertheless the CP-7 calculation still has its right to exist because it can better predict other quantities than energy, for example the electric transition dipole moment.

Moving forward, we could definitely improve are our free-ion wave functions. The easiest thing would be finding a better way to solve the radial Schrödinger equation. The numerical method we have chosen is neither efficient nor accurate but it is simple. Since the wave functions vary rapidly for small r a natural choice would be a non-linear grid, i.e. a grid where the distance between two neighbouring grid points increases as r increases. Furthermore approximating the second derivatives with finite differences is quite a primitive method (2nd order error). We could use Numerov's algorithm to solve the radial Schrödinger equation for a given energy. The main reason why we did not do that is we did not know how to find the energies of the bound states for a given model potential.

Another refinement would be including a spin-orbit term in the radial Schrödinger equation as it is done in [9]. For heavy atoms such as Lutetium this is surely a recommendable adjustment.

Also, one should definitely consider using the more general model potential. The one we used is most likely not very well-adapted for Lutetium. Or one could of course use another method to find wave functions altogether. Then there is also the possibility of improving the ligand field calculation. Bencheikh and Schamps suggest that in cases involving heavy cations, when spin-orbit interactions are known to produce splitting effects that compete or are even larger than those due to the ligand field, the use of relativistic LFT (RLFT) should become mandatory. In contrast to non-relativistic LFT, their RLFT treatment includes relativistic interactions in the Hamiltonian of the free metallic ions so that spin-orbit effects are accounted for at the basic level of the theory [19].

6 Conclusion

The ligand field approach by RMF has allowed us to calculate the energies of the three lowest excited states of four different molecules. The strength of these calculations lies in their simplicity. They yield good results for a first estimate. The only challenging task is the computation of the free-ion wave functions. Within the framework of this project we have decided to use the Klapisch model potential approach to calculate these functions. We have managed to calculate the energies of CaF with comparable accuracy as RMF. For LuO the quality of our results decreased to some degree, most likely because the quality of our wave functions deteriorated. The calculation of CaOH has shown that the ligand field approach delivers good results even for molecules with the diatomic ligand OH⁻. At the end we calculated the ligand field energy levels of LuOH⁺ and made an estimate for the A-X transition based on what we have learned from the other three molecules.

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