tive electrons in the crystal. These electrons are not free. They are submitted to the crystalline potential, to interactions with other electrons which give rise to some localization. This is the Hund-Mulliken type approach.

These two approaches are used in magnetism. The first one is frequently used for insulating materials whereas the second one is frequently used for metals. On the basis of the simplest point-charge ionic model the electrostatic potential $V(r, \theta, \varphi)$ due to the surrounding point charges at a point (r, θ, φ) near the origin is :

$$V(r, \theta, \varphi) = \sum_j \frac{q_j}{|\vec{R}_j - \vec{r}|}$$

where q_j is the charge at the j^{th} neighboring ion, at distance $\vec{R}_j$ from the origin. If the magnetic ion has a charge q_i at $(r_i, \theta_i, \varphi_i)$ then the perturbing crystalline potential energy will be

$$W_c = \sum_i q_i V_i = \sum_i \frac{q_j q_i}{|\vec{R}_j - \vec{r}_i|}$$

where V should satisfy the Laplace equation. Symmetry considerations provide some help to study cristalline potential since this potential possesses the symmetry of the crystalline charge distribution.

Crystalline fields affects often iron group ions and rare earth group ions on a different way, since major energy,

is in the first case crystalline field energy, and in the second case spin orbit-coupling.

Consider a single electron with L = 1 in an orthorombic ($a \neq b \neq c$; $\alpha = \beta = \gamma = \pi/2$) crystalline potential. The crystalline energy is then

$$W_c = Ax^2 + By^2 - (A + B) z^2$$

Where A and B are functions of interatomic distances.

The ground state consists of 3 magnetic sub-levels. The three wave functions

$$U_x = z\, f(r)$$
$$U_y = y\, f(r)$$
$$U_z = z\, f(r)$$

are orthogonal. We suppose they are normalized. They have the property

$$(\vec{L}^2)_{op} U_i = l(l+1) U_i = 2\, U_i$$

(non diagonal elements vanish). These levels do not lead to orbital moments (See for instance $\langle U_x | L_z | U_x \rangle = -i \int \ldots \times \frac{\partial}{\partial \varphi} U_x\, dx\, dy\, dz$ = imaginary number). We have $\langle U_x | L_x | U_x \rangle = \langle U_x | L_y | U_x \rangle = 0$, too. This is known as quenching. Time average of the magnetic orbital moment is zero. Suppose U_x is the ground state orbital wave function. For S = 1/2 there are 2 possible spin state $S_z = \pm 1/2$ (→ spin functions α and β).