quadrupole interaction: miscellaneous topics

www. hyperfinecourse .org

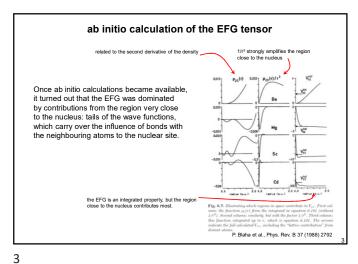
ab initio calculation of the EFG tensor

- · Calculating the EFG tensor for a real solid requires good knowledge of its
- · This was too complicated to calculate for a long time.
- Therefore, a dramatic approximation was frequently used; the point charge model replace the continuous electron density by positive point charges at the atomic sites calculate the EFG tensor due to this set of classical charges
- the (initially spherical) charge distribution of the atom at r=0 gets deformed by this external EFG. This provides an additional EFG, proportional to the external one. The proportionality factor (Sternheimer antishielding factor) can be estimated from ab initio calculations on free ions
- an extra proportionality due to an EFG by unfilled orbitals of the atom at r=0 is present as well

$$V_{zz} = (1 - K) (1 - \gamma_{\infty}) V_{zz}^{latt}$$

Very crude, but there was nothing better and many people strongly believed in this for decades. However, it doesn't really give much insight.

2



Temperature dependence of the EFG tensor Summary of experimental observations: $V_{zz}(T) = V_{zz}(0)(1-BT^{\alpha})$ 111Cd in Cd with spd-electrons, very often α≈1.5 with f-electrons, very often $\alpha \approx 1.0$ sometimes more complicate behaviour appears 100 200 300 400 500 600 T (K)

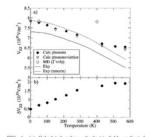
Temperature dependence of the EFG tensor

Long-standing question : is there an analytical argument for the α =1.5 ?

ab initio study of thermally induced vibrations for Cd in hcp-Cd (supercell with 24 atoms) : the order of magnitude is recovered.

Prohibitively long calculations on cells with 2000 atoms would be needed to get good numerical accuracy

→ this strongly suggests the 1.5 exponent is the average of many harmonic modes, and is more accidental than analytical.



perature (triangles), compared with experiment. MD results at 50 K and 400 K (circles) are rescaled so that the 50 K result matches the experimental value. (b) The standard deviation of the 9×24

D. Torumba et al., Phys. Rev. B 74 (2006) 144304

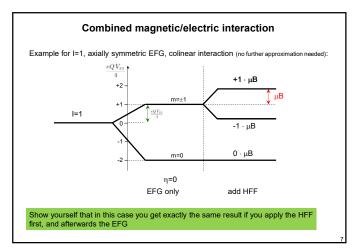
4

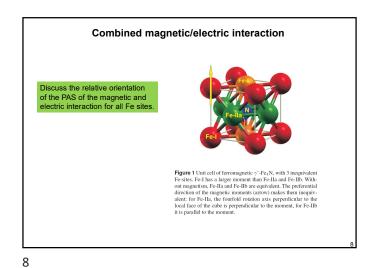
6

Combined magnetic/electric interaction

- •The formalism remains the same as before
 - · write the combined hamiltonian
 - find all matrix elements (degenerate 1st order perturbation)
 - diagonalize the matrix to find eigenvalues
- · The general case can be technically involved, but important simpler situations exist:
 - if one of the two interactions is much stronger than the other one, consider the weak interaction as a new perturbation (i.e. you work in the PAS of the dominant interaction)
 - in all cases, expressions are simpler for an axially symmetric EFG
 - the case where the magnetic hyperfine field is aligned with the z-axis of the PAS of the EFG (i.e. the magnetic and electric PAS coincide) can be treated

5





An extended nucleus What did we have for the monopole term of the charge-charge interaction: quasi moment quasi momen / quasi field $\tilde{M}^{(2)} \propto \{r^4Y_{00}\}$ $\tilde{V}^{(2)} \propto \Delta^2 v(0)$ $\tilde{Q}^{(2)} \propto \{r^6Y_{20}\}$ $\tilde{V}^{(2)}_{ij} \propto \partial_{ij}\Delta^2 v(0)$ O(0) MI [a] $MS^{(2)}$ $\left. egin{aligned} Q \propto r^2 Y_{20} \\ V_{ij} \propto \partial_{ij} v(0) \end{aligned} \right\} \, \mathrm{QI} \, [\mathrm{b}]$ QS(2) $\mathcal{O}(2)$ $QS^{(1)}$ [e] $H \propto r^4 Y_{40}$ $V_{ijkl} \propto \partial_{ijkl} v(0)$ HDI [c] HDS⁽¹⁾ $\mathcal{O}(4)$ HDS(2) c) An extra potential at the nucleus, that depends on nuclear properties and on a point property of the electron system tmA

An extended nucleus Analogous effect for the quadrupole term: multipole / quasi field $\tilde{M}^{(1)} \propto \{r^2 Y_{00}\}$ $\}$ $MS^{(1)}$ [d] $M \propto r^{0}Y_{00}$ $V \propto v(0)$ MI [a] 02(0) $MS^{(2)}$ $Q \propto r^2 Y_{20}$ $V_{ij} \propto \partial_{ij} v(0)$ QI [b] $QS^{(2)}$ $\mathcal{O}(2)$ $H \propto r^4 Y_{40}$ $V_{ijkl} \propto \partial_{ijkl} v(0)$ HDI [c] HDS⁽¹⁾ $\mathcal{O}(4)$ HDS⁽²⁾ d) An extra EFG at the nucleus, that depends on nuclear properties and on a point property of the electron system tmB

10

9

An extended nucleus Analogous effect for the quadrupole term: quasi momen / quasi field $\tilde{M}^{(1)} \propto \{r^2 Y_{00}\}$ $MS^{(1)}$ [d] $M \propto r^0 Y_{00}$ $V \propto v(0)$ MI [a] 0(0) $MS^{(2)}$ $Q \propto r^2 Y_{20}$ $V_{ij} \propto \partial_{ij} v(0)$ PI [b] QS(2) 0(2) $\left. egin{aligned} H \propto r^4 Y_{40} \\ V_{ijkl} \propto \partial_{ijkl} v(0) \end{aligned} \right\} \text{ HDI [c]}$ HDS(1) $\mathcal{O}(4)$ HDS(2) d) An extra EFG at the nucleus, that depends on nuclear properties and on a point property of the electron system tmB Very small! K. Koch et al. Phys. Rev. A 81 (2010) 032507 http://dx.doi.org/10.1103/PhysRevA.81.032507 K. Rose and SC, Phys. Chem. Chem. Phys. 14 (2012) 11308 http://dx.doi.org/10.1039/c2cp40740j

11