

quadrupole interaction : miscellaneous topics

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ab initio calculation of the EFG tensor

- Calculating the EFG tensor for a real solid requires good knowledge of its electron density.
- 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 (Sterneimer 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.

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ab initio calculation of the EFG tensor

related to the second derivative of the density $\rho_{zz}(r) \propto \nabla^2 \rho(r)$

$1/r^2$ strongly amplifies the region close to the nucleus

Once ab initio calculations became available, it turned out that the EFG was dominated by contributions from the region very close to the nucleus: tails of the wave functions, which carry over the influence of bonds with the neighbouring atoms to the nuclear site.

the EFG is an integrated property, but the region close to the nucleus contributes most.

Fig. 6.7. Illustrating which regions in space contribute to V_{zz} . First column: the function $\rho(r)$ from the integrated in equation 6.101 (without $1/r^2$). Second column: similarly, but with the factor $1/r^2$. Third column: the function integrated up to r , which is equation 6.101. The arrows indicate the full calculated V_{zz} , including the "lattice contribution" from distant atoms.

P. Blaha et al., Phys. Rev. B 37 (1988) 2792

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Temperature dependence of the EFG tensor

Summary of experimental observations:

$$V_{zz}(T) = V_{zz}(0)(1 - BT^{\alpha})$$

with spd-electrons, very often $\alpha \approx 1.5$

with f-electrons, very often $\alpha \approx 1.0$

sometimes more complicate behaviour appears

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Temperature dependence of the EFG tensor

Long-standing question : is there an analytical argument for the $\alpha=1.5$?

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.

FIG. 6. (a) Calculated values of electric-field gradient for hcp-Cd as a function of temperature: for a fixed lattice constant (diamonds) and for the lattice constant corresponding to that temperature (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 $9 \times 24 = 216$ V_{zz} values as a function of temperature.

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

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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 exactly.

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Combined magnetic/electric interaction

Example for $I=1$, axially symmetric EFG, colinear interaction (no further approximation needed):

Show yourself that in this case you get exactly the same result if you apply the HFF first, and afterwards the EFG

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Combined magnetic/electric interaction

Discuss the relative orientation of the PAS of the magnetic and electric interaction for all Fe sites.

Figure 1 Unit cell of ferromagnetic γ -Fe₄N, with 3 inequivalent Fe-sites. Fe-I has a larger moment than Fe-IIa and Fe-IIb. Without magnetism, Fe-IIa and Fe-IIb are equivalent. The preferential direction of the magnetic moments (arrow) makes them inequivalent: for Fe-IIa, the fourfold rotation axis perpendicular to the local face of the cube is perpendicular to the moment, for Fe-IIb it is parallel to the moment.

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An extended nucleus

What did we have for the monopole term of the charge-charge interaction:

order	multipole moment / field		first order quasi moment / quasi field		second order quasi moment / quasi field	
$\mathcal{O}(0)$	$M \propto r^0 Y_{00}$ $V \propto v(0)$	MI [a]	$M^{(1)} \propto \{r^2 Y_{00}\}$ $V^{(1)} \propto \Delta v(0)$	MS ⁽¹⁾ [d]	$M^{(2)} \propto \{r^4 Y_{00}\}$ $V^{(2)} \propto \Delta^2 v(0)$	MS ⁽²⁾ ...
$\mathcal{O}(2)$	$Q \propto r^2 Y_{20}$ $V_{ij} \propto \partial_{ij} v(0)$	QI [b]	$Q^{(1)} \propto \{r^4 Y_{20}\}$ $V_{ij}^{(1)} \propto \partial_{ij} \Delta v(0)$	QS ⁽¹⁾ [e]	$Q^{(2)} \propto \{r^6 Y_{20}\}$ $V_{ij}^{(2)} \propto \partial_{ij} \Delta^2 v(0)$	QS ⁽²⁾ ...
$\mathcal{O}(4)$	$H \propto r^4 Y_{40}$ $V_{ijkl} \propto \partial_{ijkl} v(0)$	HDI [c]	$H^{(1)} \propto \{r^6 Y_{40}\}$ $V_{ijkl}^{(1)} \propto \partial_{ijkl} \Delta v(0)$	HDS ⁽¹⁾	$H^{(2)} \propto \{r^8 Y_{40}\}$ $V_{ijkl}^{(2)} \propto \partial_{ijkl} \Delta^2 v(0)$	HDS ⁽²⁾ ...

c) **tmA** An extra potential at the nucleus, that depends on nuclear properties and on a point property of the electron system

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An extended nucleus

Analogous effect for the quadrupole term:

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An extended nucleus

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d) **tmB** An extra EFG at the nucleus, that depends on nuclear properties and on a point property of the electron system

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/c2cp40740g>

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