Katrin Koch, Klaus Koepernik,
Dimitri Van Neck, Helge Rosner, Stefaan Cottenier

Electron Penetration into the Nucleus and its Effect on the Quadrupole Interaction

HFI/NQI 2010

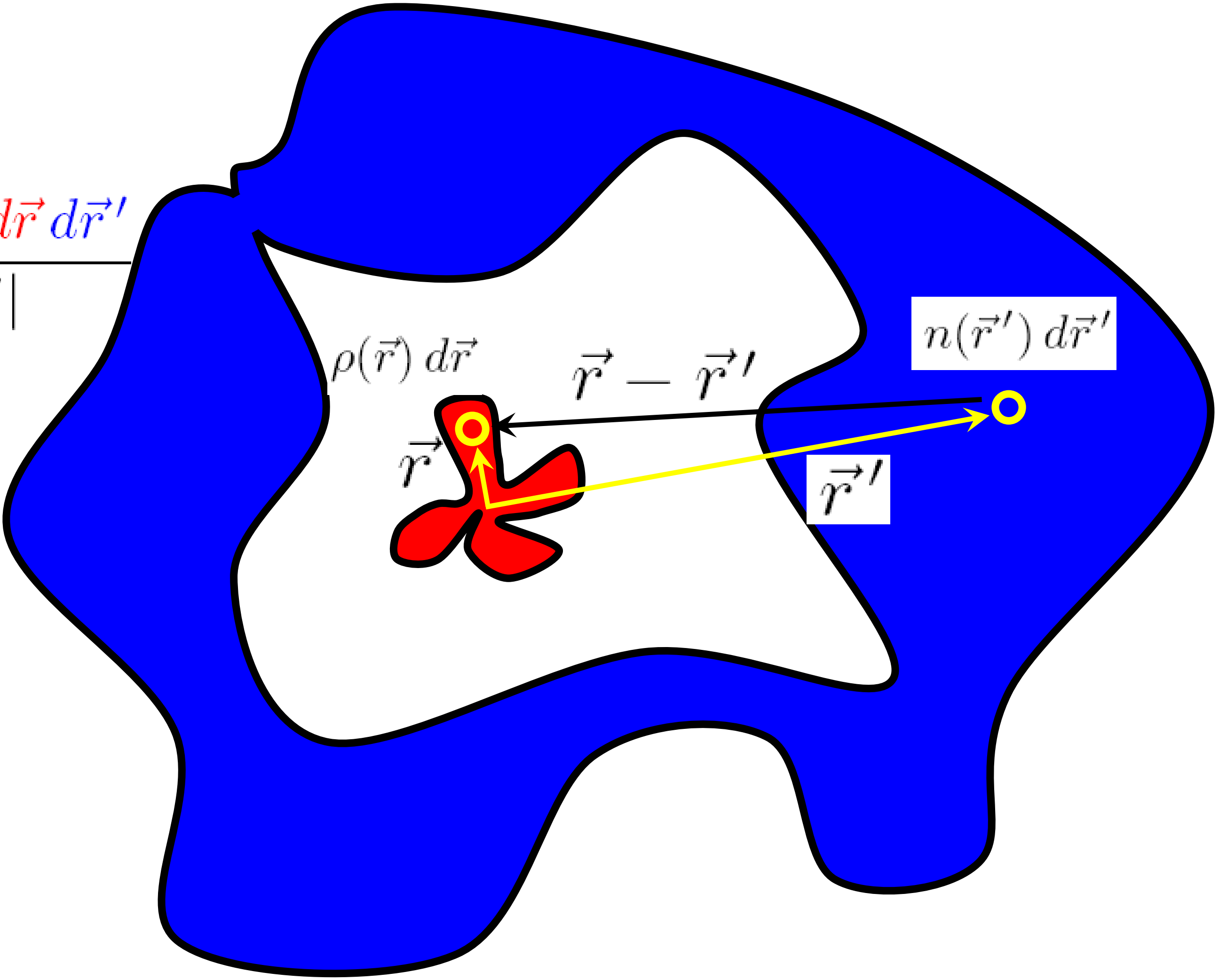
Content

- The formalism
  - → quadrupole interaction ❶
  - → quadrupole shift
- Toy model
  - → quadrupole interaction
  - → quadrupole shift
- Experimental consequences
  - ➔ quadrupole anomaly

$$dE = \frac{1}{4\pi\epsilon_0} \frac{[\rho(\vec{r})\, d\vec{r}]\ \ [n(\vec{r}')\, d\vec{r}']}{|\vec{r}-\vec{r}'|}$$

⇩

$$E = \frac{1}{4\pi\epsilon_0} \int\int \frac{\rho(\vec{r})\, n(\vec{r}')\, d\vec{r}\, d\vec{r}'}{|\vec{r}-\vec{r}'|}$$



$$E = \frac{1}{4\pi\epsilon_0}\int\int\frac{\rho(\vec{r})n(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}d\vec{r}d\vec{r}\,'$$ ⇨ complicated ...

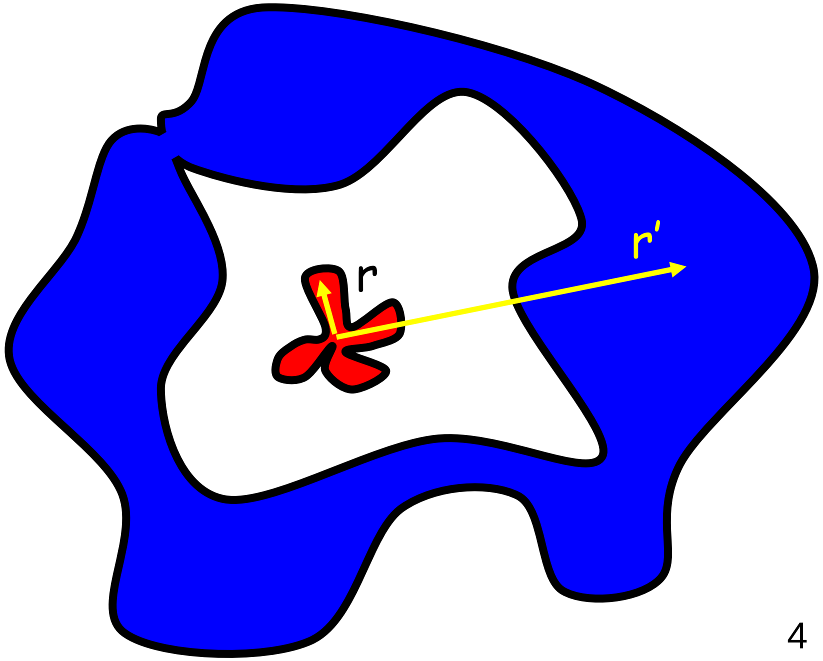
$$\frac{1}{|\vec{r}-\vec{r}\,'|} = \sum_{l,m}\frac{4\pi}{2l+1}\frac{r_<^l}{r_>^{l+1}}Y^*_{l,m}(\Omega)Y_{l,m}(\Omega')$$

$$E = \sum_{l,m}\overset{\text{nucleus}}{Q^*_{lm}}\,\overset{\text{electrons}}{V_{lm}}$$

$$\boxed{\begin{aligned} r_< &\equiv r \\ r_> &\equiv r\,' \end{aligned}}$$

$$Q_{lm} = \sqrt{\frac{4\pi}{2l+1}}\int r^l\rho(\vec{r})Y_{lm}(\Omega)d\vec{r}$$

$$V_{lm} = \frac{1}{4\pi\epsilon_0}\sqrt{\frac{4\pi}{2l+1}}\int\frac{1}{r'^{l+1}}n(\vec{r}\,')\,Y_{lm}(\Omega')\,d\vec{r}\,'$$



$$E = \frac{1}{4\pi\epsilon_0}\int\int\frac{\rho(\vec{r})n(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}d\vec{r}d\vec{r}\,'$$

→ complicated ...

$$\frac{1}{|\vec{r}-\vec{r}\,'|} = \sum_{l,m}\frac{4\pi}{2l+1}\frac{r_<^l}{r_>^{l+1}}Y^*_{l,m}(\Omega)Y_{l,m}(\Omega')$$

$$\boxed{\begin{aligned} r_< &\equiv r \\ r_> &\equiv r\,' \end{aligned}}$$

$$E = \sum_{l,m}\overset{\text{nucleus}}{Q^*_{lm}}\overset{\text{electrons}}{V_{lm}}$$

	l=0	~~l=1~~	l=2
nucleus	charge	~~dipole moment~~	quadrupole moment
electrons	electric potential	~~electric field~~	electric-field gradient (EFG)
	(scalar)	*(vector)*	*(rank 2 tensor)*

$$Q_{lm} = \sqrt{\frac{4\pi}{2l+1}}\int r^l\rho(\vec{r})Y_{lm}(\Omega)d\vec{r}$$

$$V_{lm} = \frac{1}{4\pi\epsilon_0}\sqrt{\frac{4\pi}{2l+1}}\int\frac{1}{r'^{l+1}}n(\vec{r}\,')\,Y_{lm}(\Omega')\,d\vec{r}\,'$$

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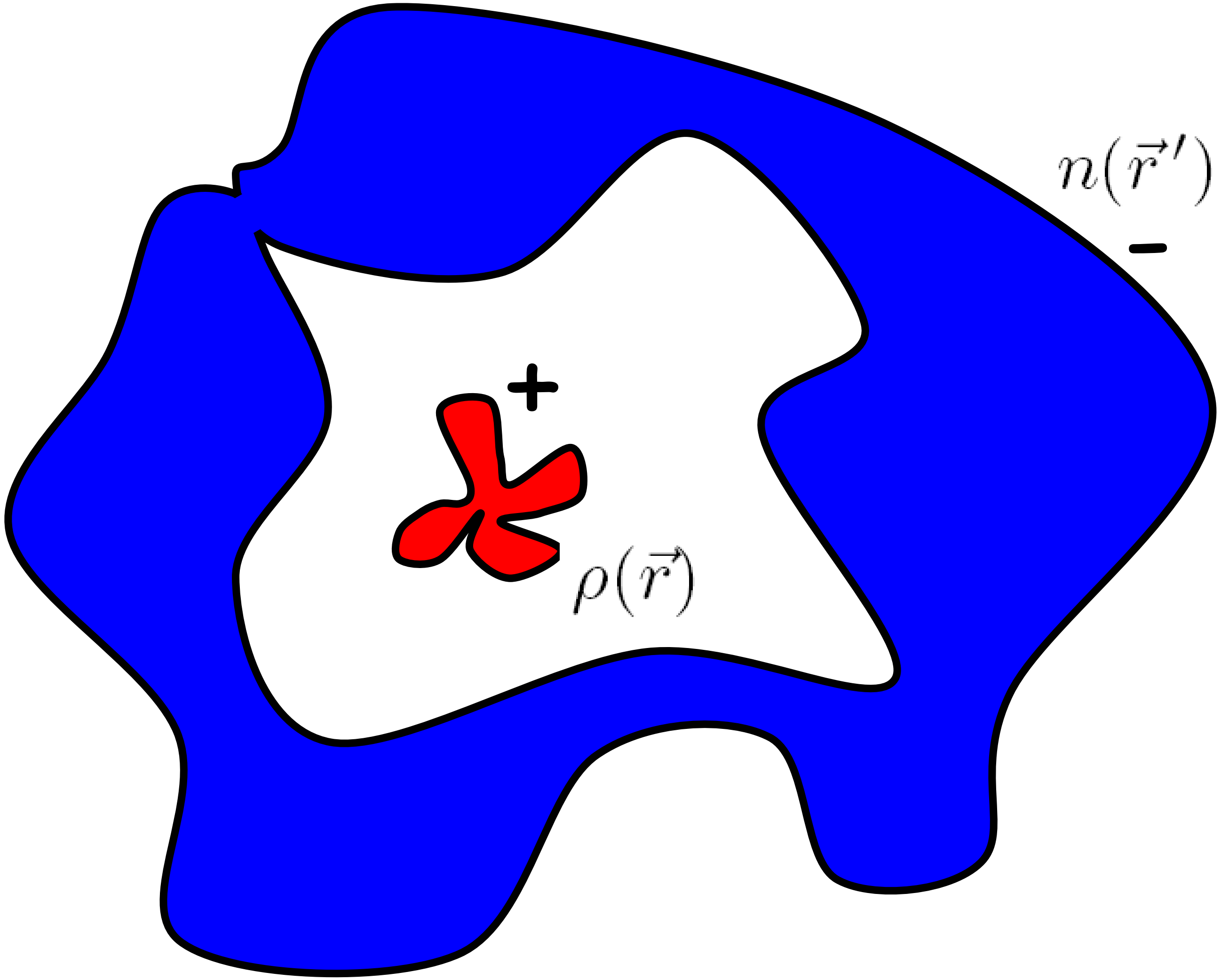
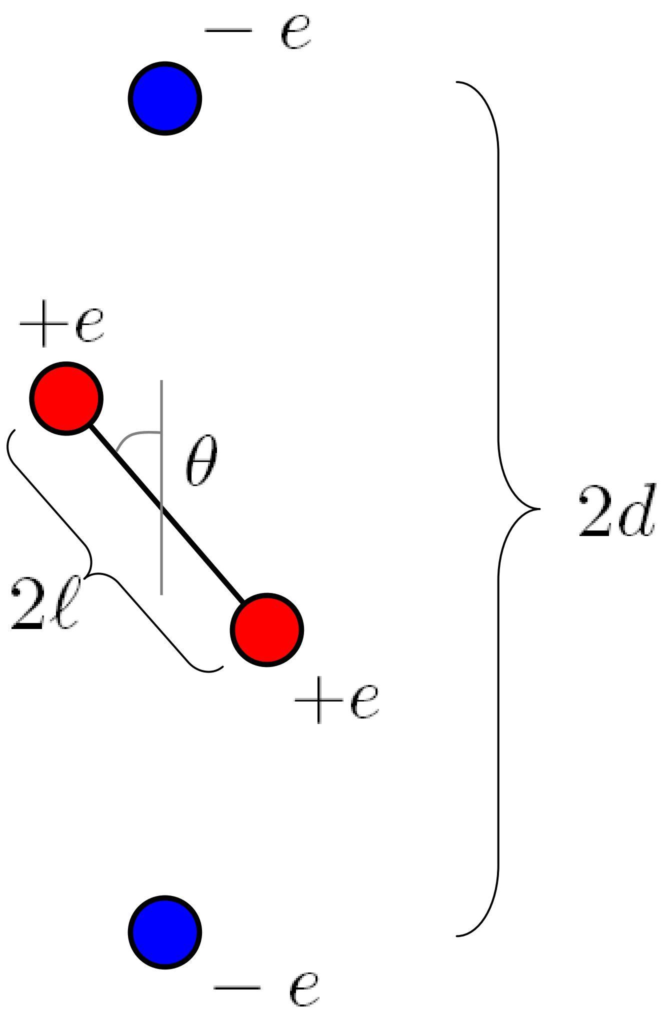
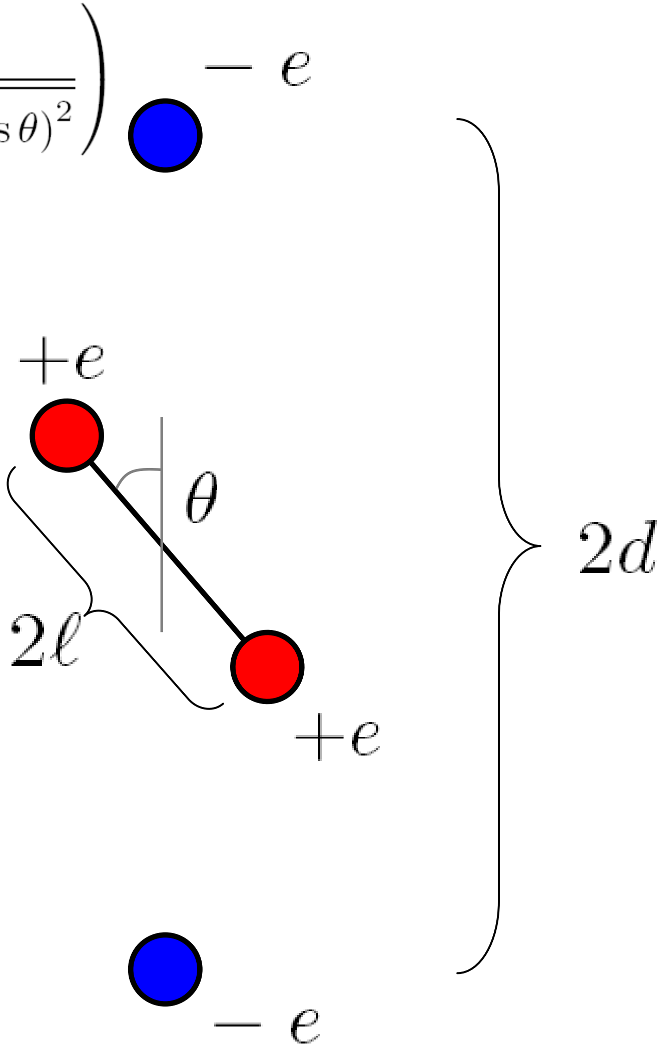
  ➔ quadrupole anomaly


$n(\vec{r}')$
$-$
$+$
$\rho(\vec{r})$

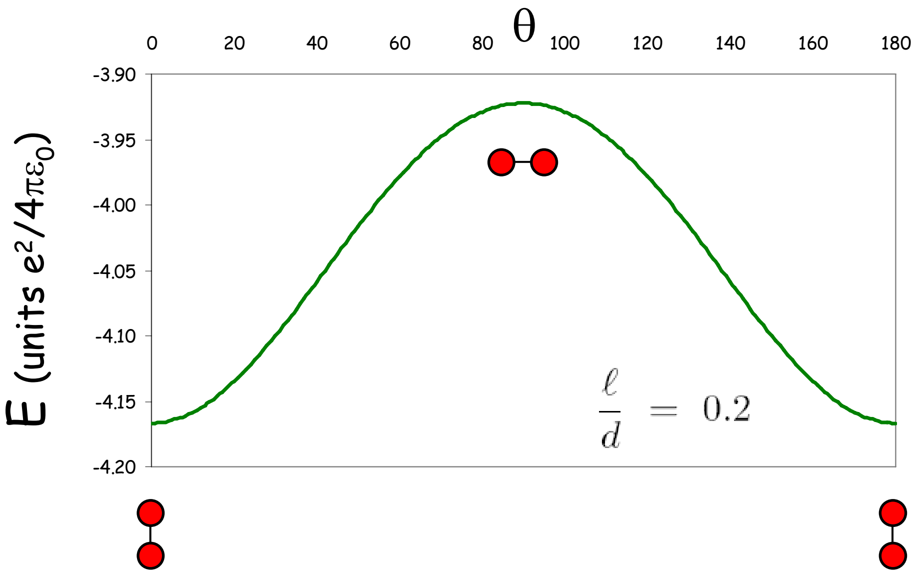

$-\ e$
$+e$
θ
2ℓ
$+e$
$2d$
$-\ e$

Exact solution :

$$E = \left(\frac{1}{4\pi\epsilon_0}\right)\left(\frac{-2e^2}{\sqrt{\ell^2\sin^2\theta+(d-\ell\cos\theta)^2}}+\frac{-2e^2}{\sqrt{\ell^2\sin^2\theta+(d+\ell\cos\theta)^2}}\right)$$

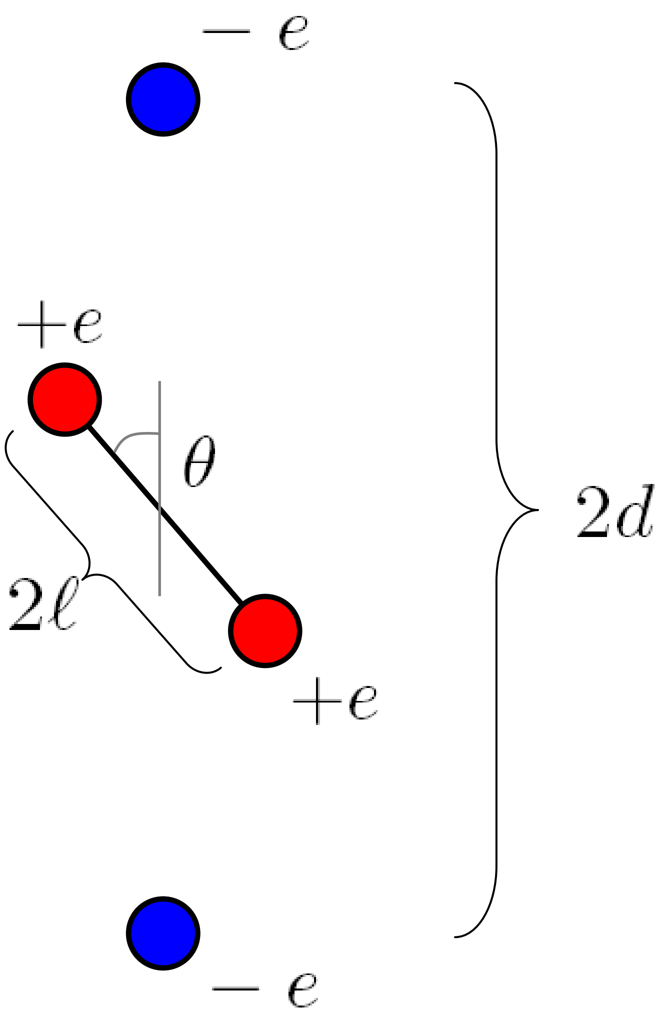


exact solution:

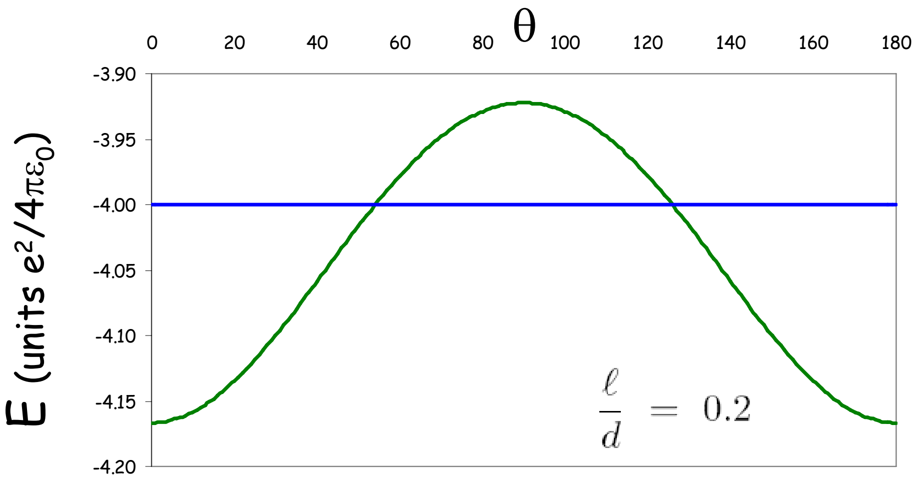


Monopole contribution :

$$E_0 = \frac{1}{4\pi\epsilon_0}\frac{-4e^2}{d}$$



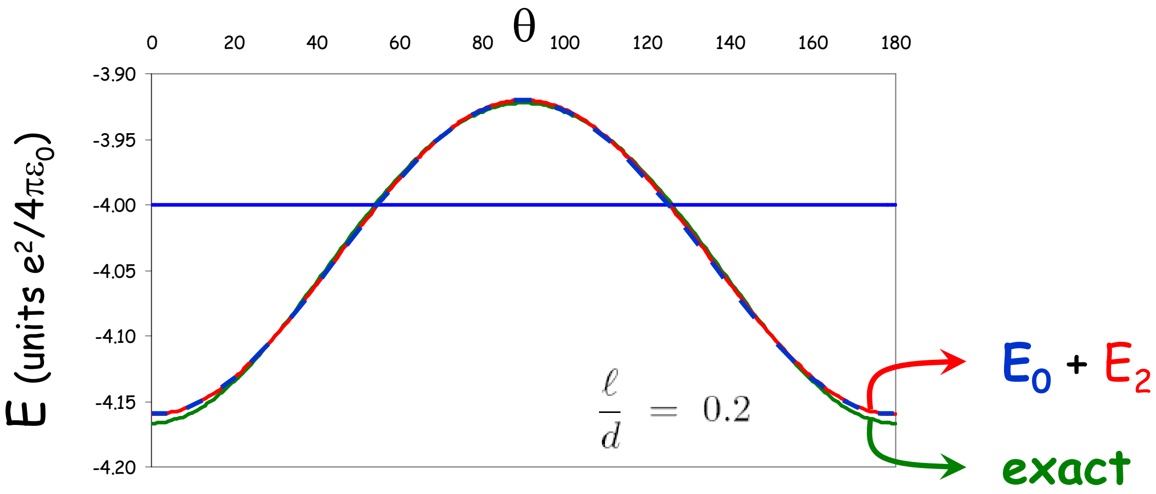
base-line = monopole interaction

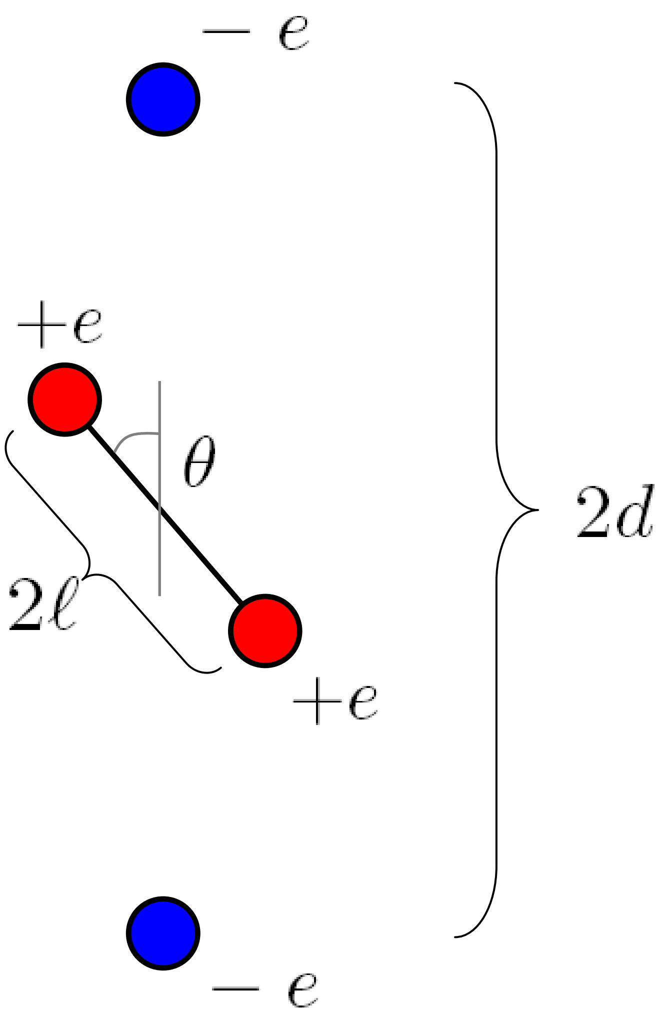


Quadrupole contribution :

$$E_2 \;=\; \frac{1}{4\pi\epsilon_0}\,\frac{-2e^2\ell^2}{d^3}\;\left(2\cos^2\theta-\sin^2\theta\right)$$

curvature = quadrupole interaction





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$$E = \frac{1}{4\pi\epsilon_0}\int\int\frac{\rho(\vec{r})n(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}d\vec{r}d\vec{r}\,'$$

⇨ complicated ...

$$\frac{1}{|\vec{r}-\vec{r}\,'|} = \sum_{l,m}\frac{4\pi}{2l+1}\boxed{\frac{r_<^l}{r_>^{l+1}}}Y^*_{l,m}(\Omega)Y_{l,m}(\Omega')$$

$$E = \sum_{l,m}\overset{\text{nucleus}}{Q^*_{lm}}\,\overset{\text{electrons}}{V_{lm}}$$

$$\boxed{\begin{array}{lcl} r_< & \equiv & r \\ r_> & \equiv & r\,' \end{array}}$$

$$Q_{lm} = \sqrt{\frac{4\pi}{2l+1}}\int r^l\rho(\vec{r})Y_{lm}(\Omega)d\vec{r}$$

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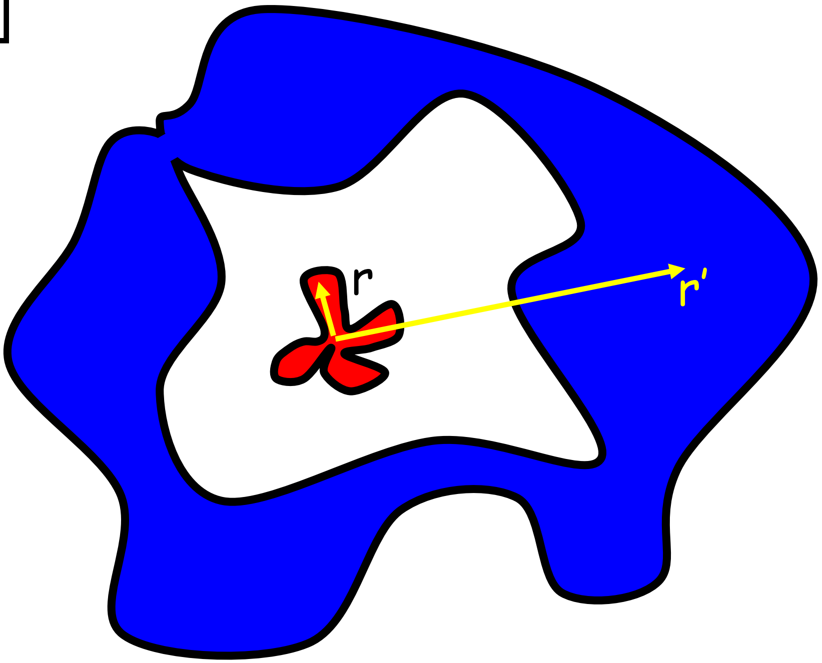

$$E = \frac{1}{4\pi\epsilon_0}\int\int \frac{\rho(\vec{r})n(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}d\vec{r}d\vec{r}\,'$$

⇒ complicated ...

$$\frac{1}{|\vec{r}-\vec{r}\,'|} = \sum_{l,m}\frac{4\pi}{2l+1}\frac{r_<^l}{r_>^{l+1}}Y^*_{l,m}(\Omega)Y_{l,m}(\Omega')$$

$$\xcancel{\boxed{\begin{array}{rcl} r_< & \equiv & r \\ r_> & \equiv & r\,' \end{array}}}$$

$$\xcancel{E = \sum_{l,m} Q^*_{lm}V_{lm}}$$

$$\xcancel{Q_{lm} = \sqrt{\frac{4\pi}{2l+1}}\int r^l\rho(\vec{r})Y_{lm}(\Omega)d\vec{r}}$$

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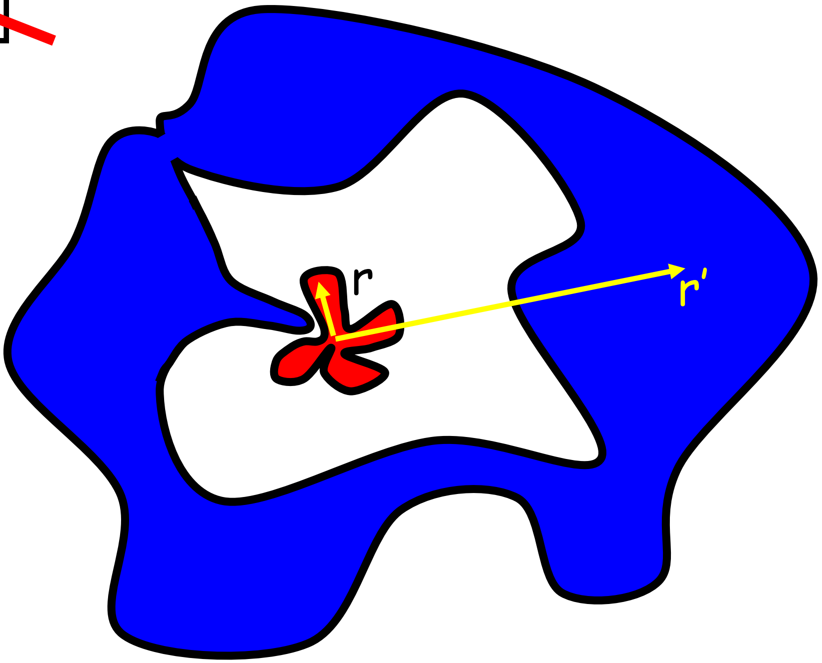

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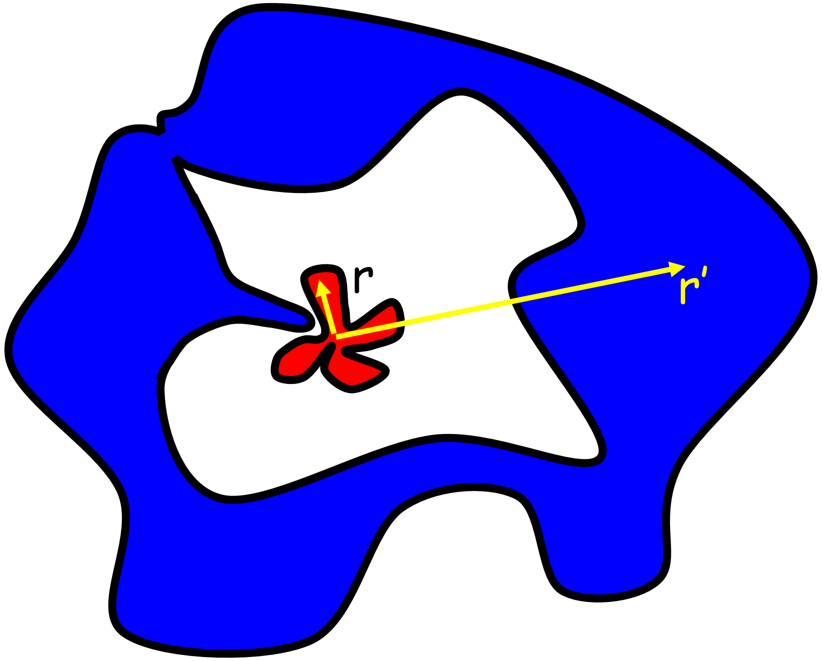
$$\frac{1}{|\vec{r}-\vec{r}\,'|} = \sum_{l,m} \frac{4\pi}{2l+1} \boxed{\frac{r_<^l}{r_>^{l+1}}} Y^*_{l,m}(\Omega) Y_{l,m}(\Omega')$$

E = E_0

+ E_2

+ ....

?

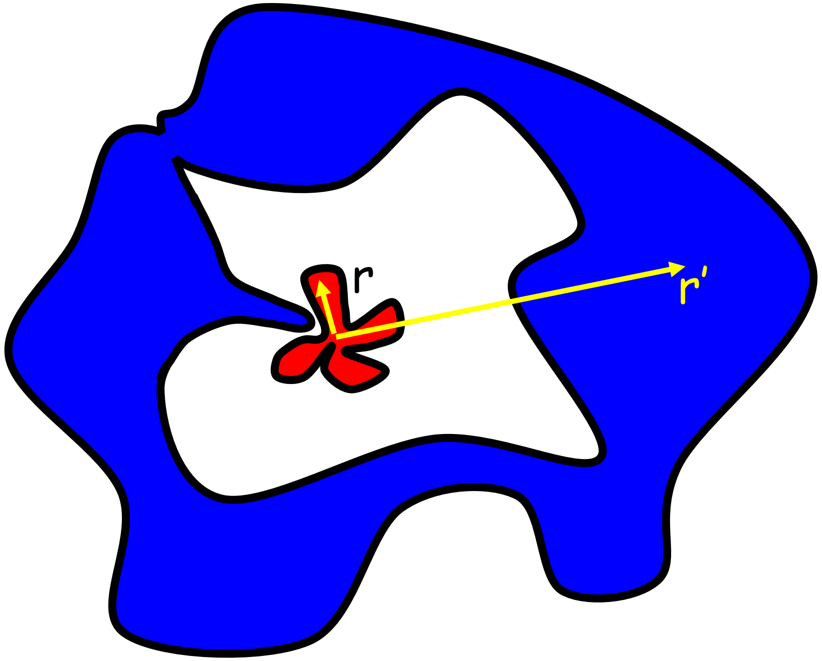


$$E = \frac{1}{4\pi\epsilon_0}\int\int\frac{\rho(\vec{r})n(\vec{r}')}{|\vec{r}-\vec{r}'|}d\vec{r}d\vec{r}'$$ ⇨ complicated ...

$$\frac{1}{|\vec{r}-\vec{r}'|} = \sum_{l,m}\frac{4\pi}{2l+1}\boxed{\frac{r_<^l}{r_>^{l+1}}}Y_{l,m}^*(\Omega)Y_{l,m}(\Omega')$$

$$\begin{aligned} E = \; & \xcancel{E_0} \\ + \; & \xcancel{E_2} \\ + \; & \ldots\ldots \end{aligned}$$

!



$$E = \frac{1}{4\pi\epsilon_0}\int\int \frac{\rho(\vec{r})n(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}\,d\vec{r}\,d\vec{r}\,'$$

⇨ complicated ...

$$\frac{1}{|\vec{r}-\vec{r}\,'|} = \sum_{l,m} \frac{4\pi}{2l+1}\boxed{\frac{r_<^l}{r_>^{l+1}}}Y^*_{l,m}(\Omega)Y_{l,m}(\Omega')$$

E = E_0 + something small

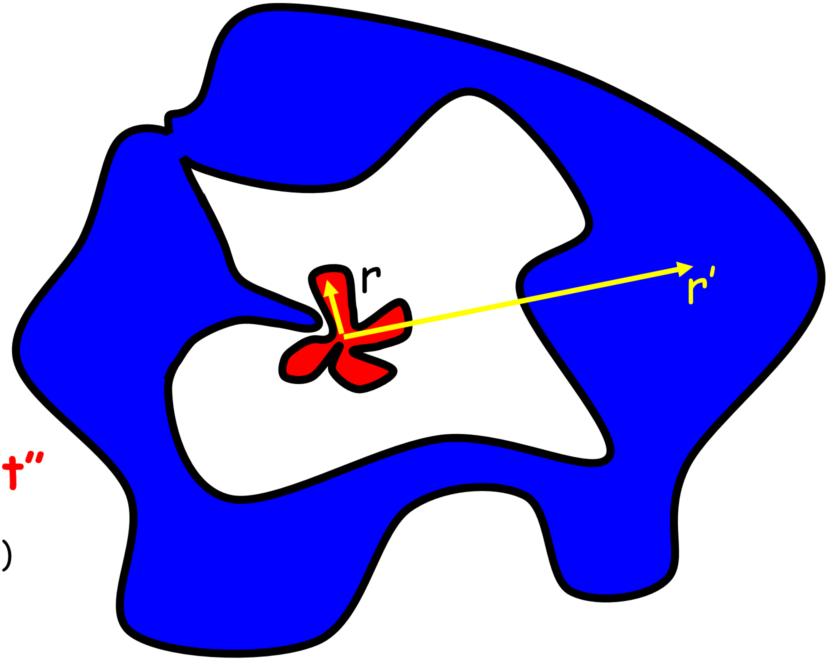
+ E_2 + something small

+ ....

"monopole shift"
(isotope shift /
isomer shift)

"quadrupole shift"

(PRA 81 (2010) 032507)



(Coord. Chem. Rev. 253 (2009) 594)

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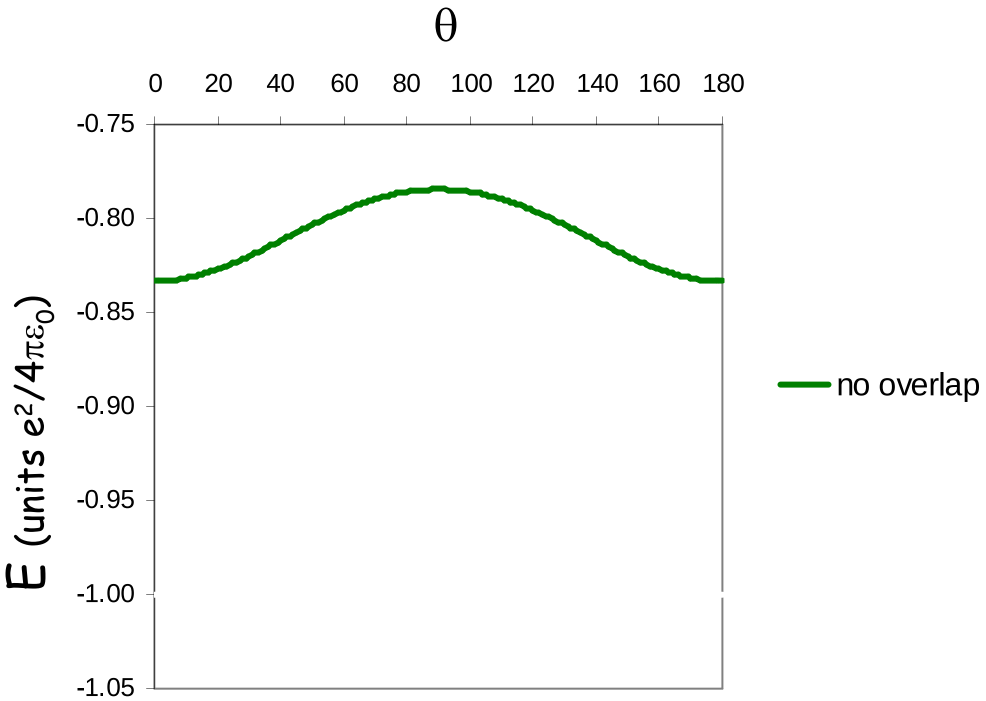
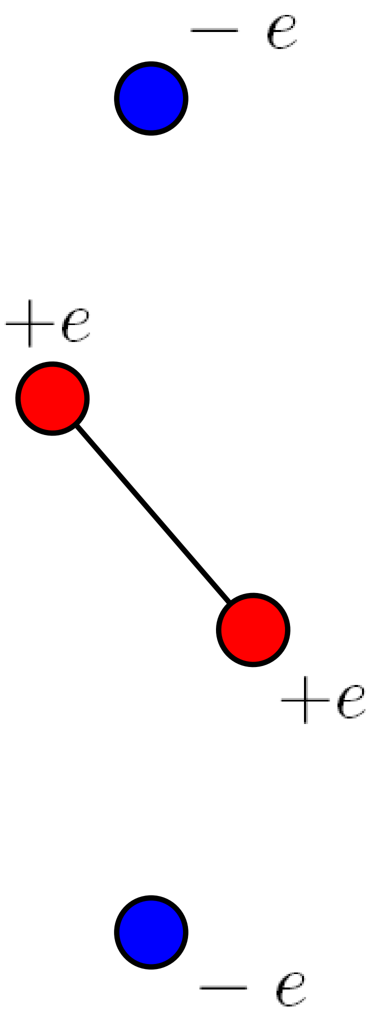
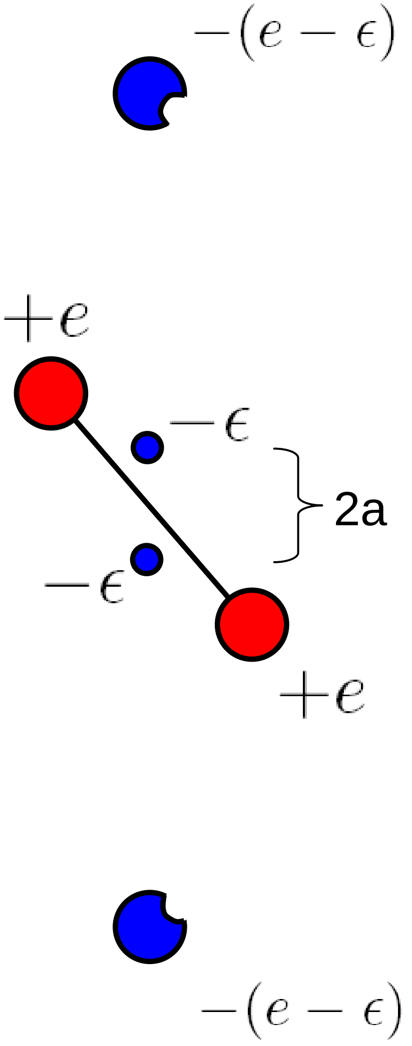
  ➔ quadrupole anomaly

Exact solution :

$$E = \left(\frac{1}{4\pi\epsilon_0}\right)\left(\frac{-2e^2}{\sqrt{\ell^2\sin^2\theta + (d-\ell\cos\theta)^2}} + \frac{-2e^2}{\sqrt{\ell^2\sin^2\theta + (d+\ell\cos\theta)^2}}\right)$$

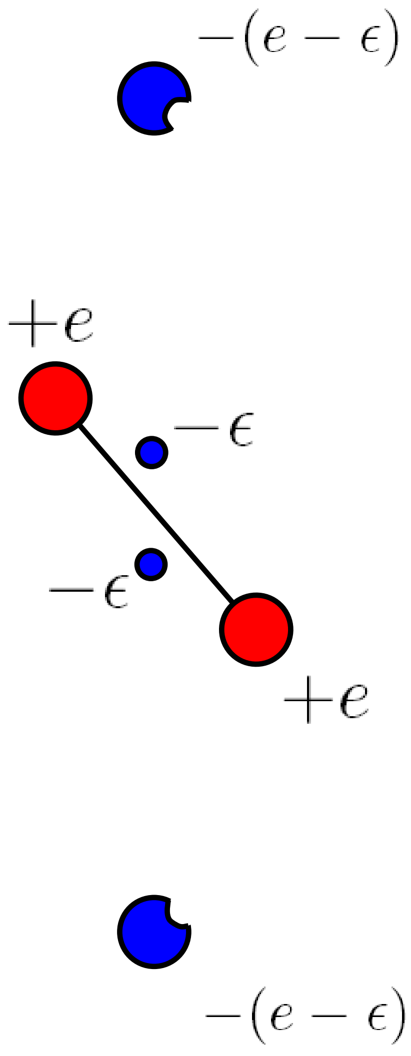


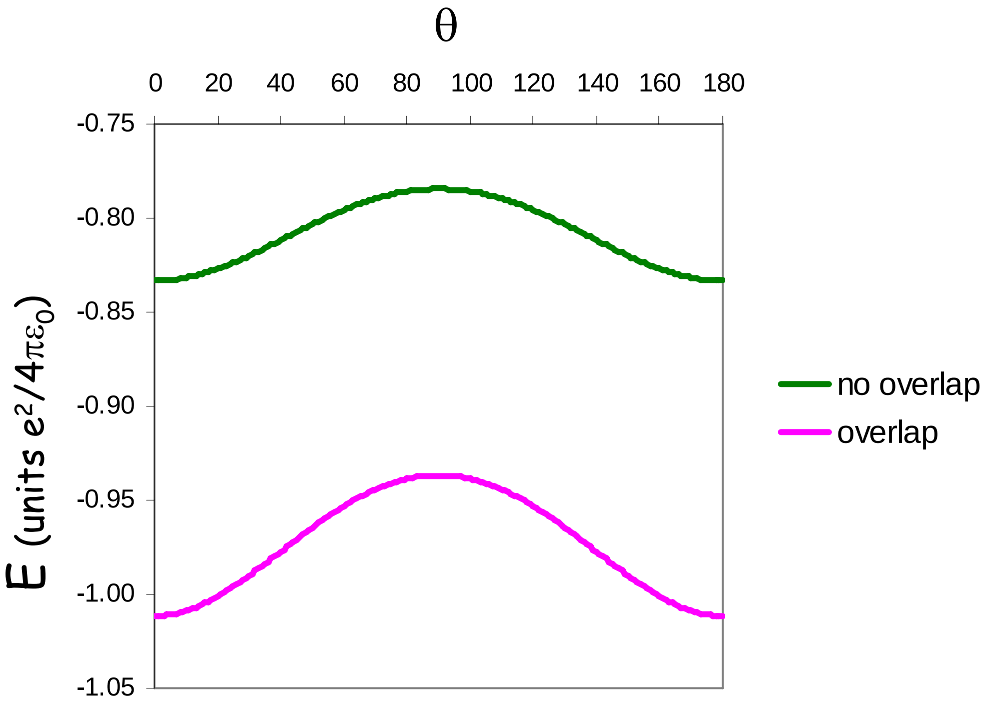


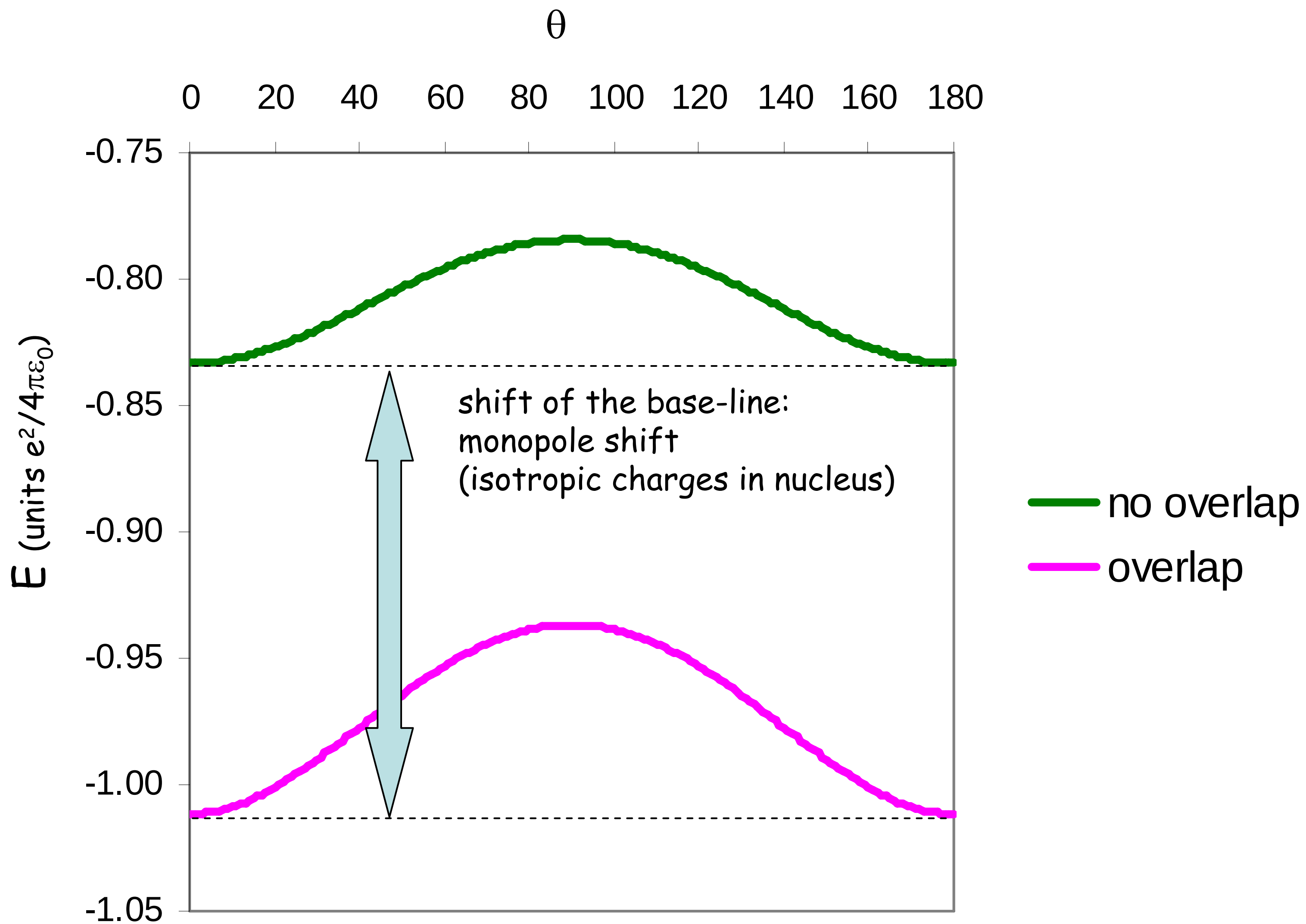

$-(e-\epsilon)$
$+e$
$-\epsilon$
2a
$-\epsilon$
$+e$
$-(e-\epsilon)$

Exact solution :

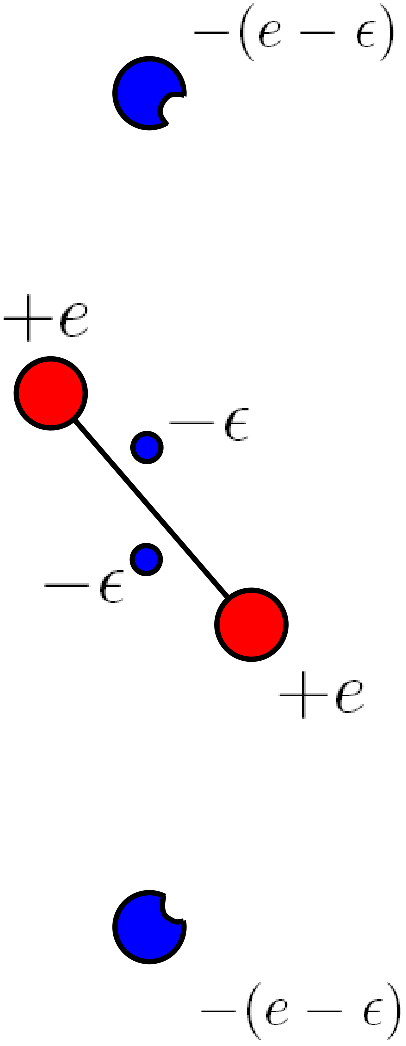
$$E(\theta) = \left(\frac{1}{4\pi\epsilon_0}\right)\left(\frac{-2e(e-\epsilon)}{\sqrt{\ell^2\sin^2\theta+(d-\ell\cos\theta)^2}}+\frac{-2e(e-\epsilon)}{\sqrt{\ell^2\sin^2\theta+(d+\ell\cos\theta)^2}}\right)$$
$$+\left(\frac{1}{4\pi\epsilon_0}\right)\left(\frac{-2\epsilon e}{\sqrt{\ell^2\sin^2\theta+(a-\ell\cos\theta)^2}}+\frac{-2\epsilon e}{\sqrt{\ell^2\sin^2\theta+(a+\ell\cos\theta)^2}}\right)$$

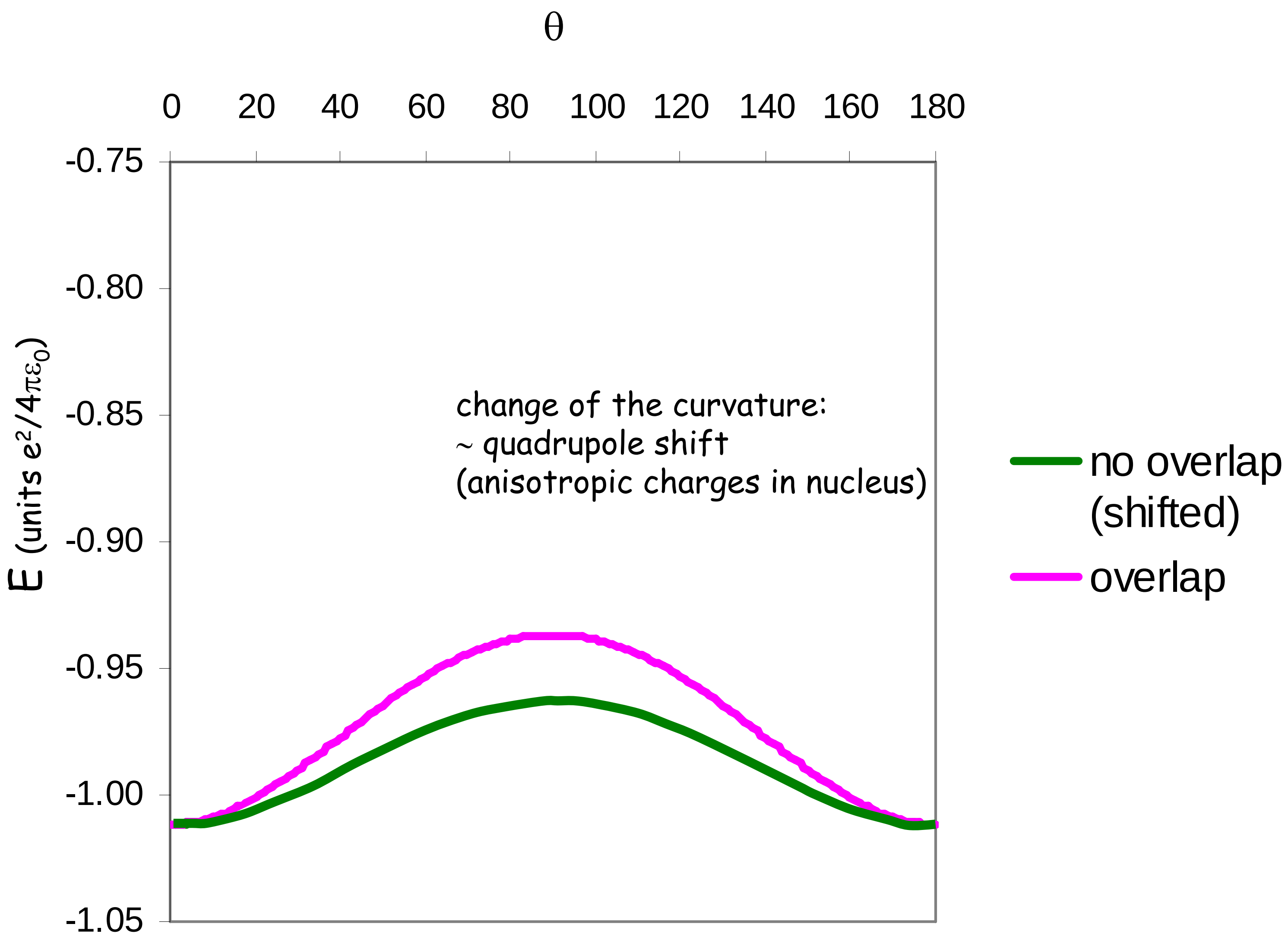




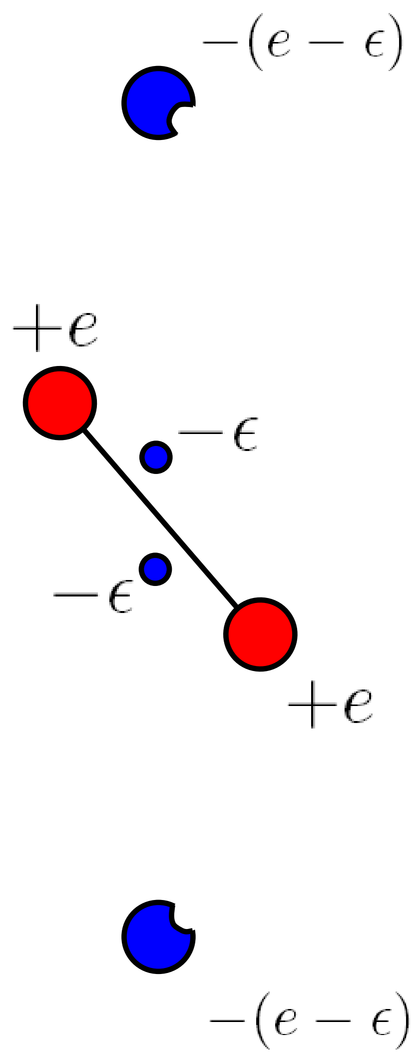


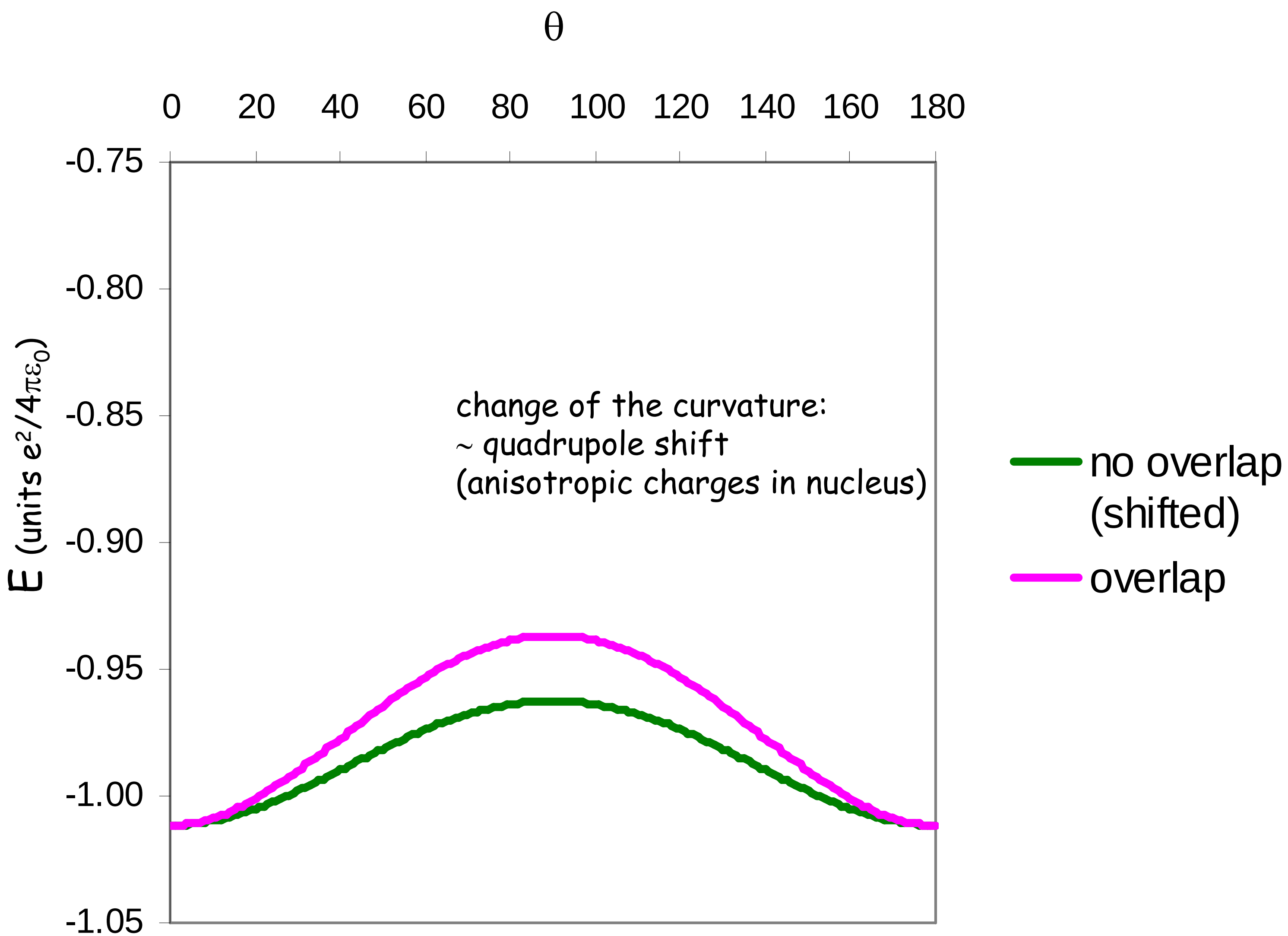
shift of the base-line:
monopole shift
(isotropic charges in nucleus)





change of the curvature:
~ quadrupole shift
(anisotropic charges in nucleus)





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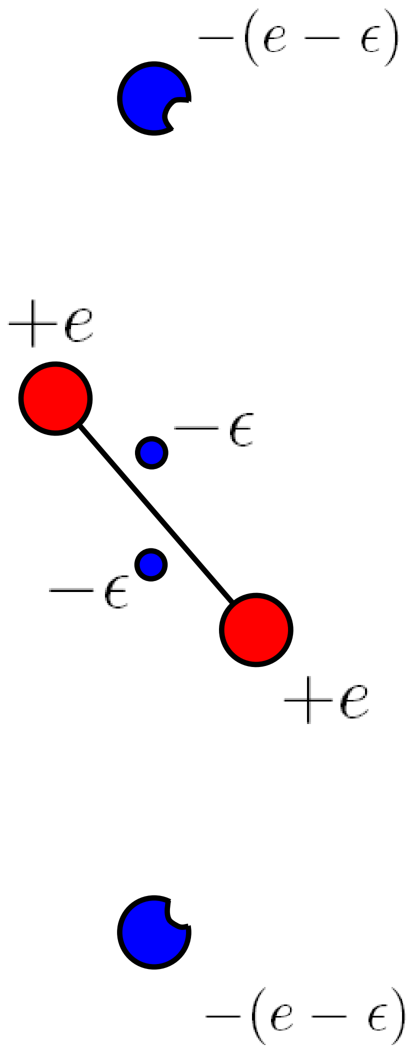
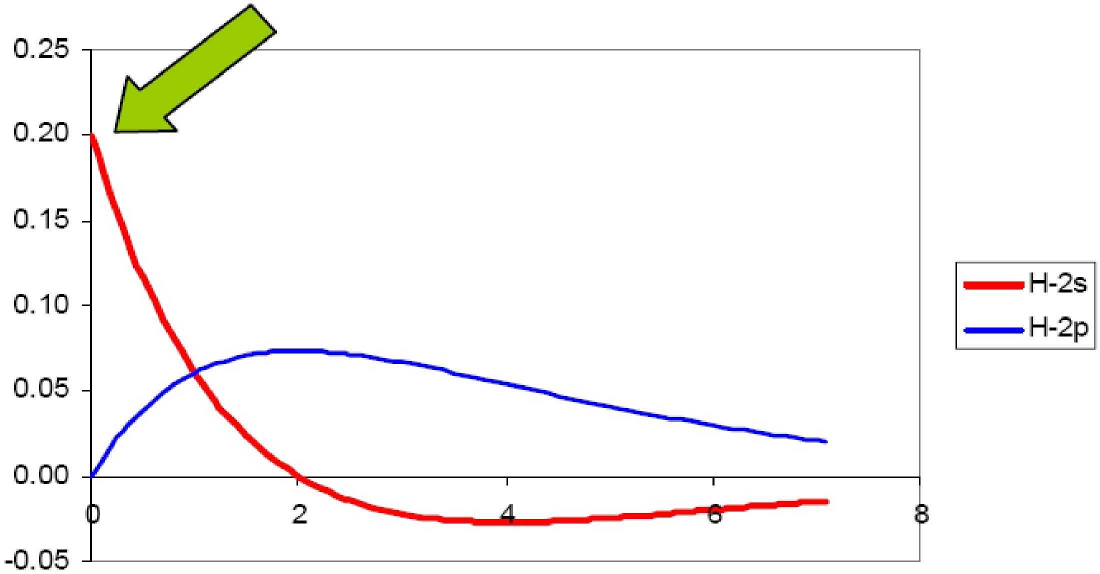


An anisotropic electron distribution
inside the nuclear volume
affects the quadrupole interaction.

	non-relativistic	relativistic
s	yes (isotropic)	yes (isotropic)
p	no	yes (anisotropic) ($p_{1/2}$)



non-relativistic H-atom radial wave functions

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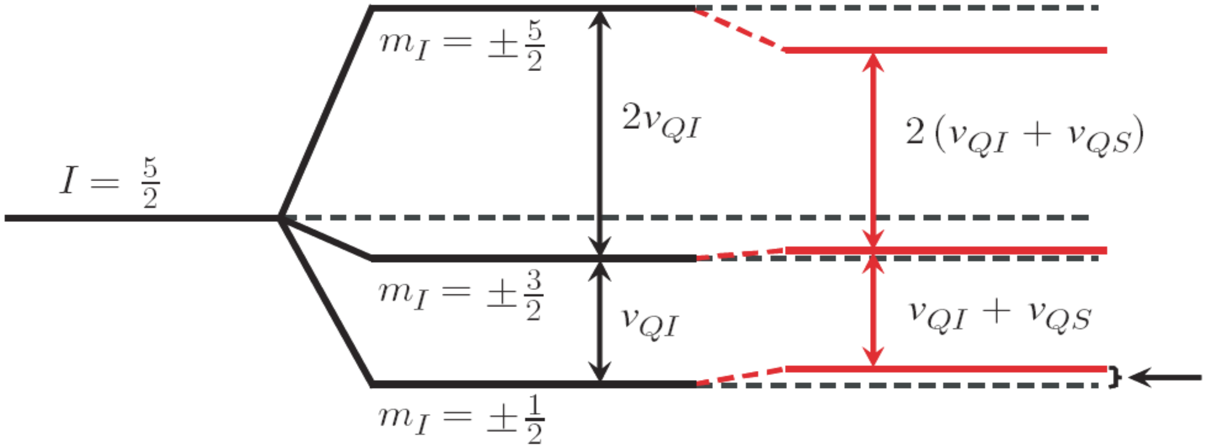
well-known

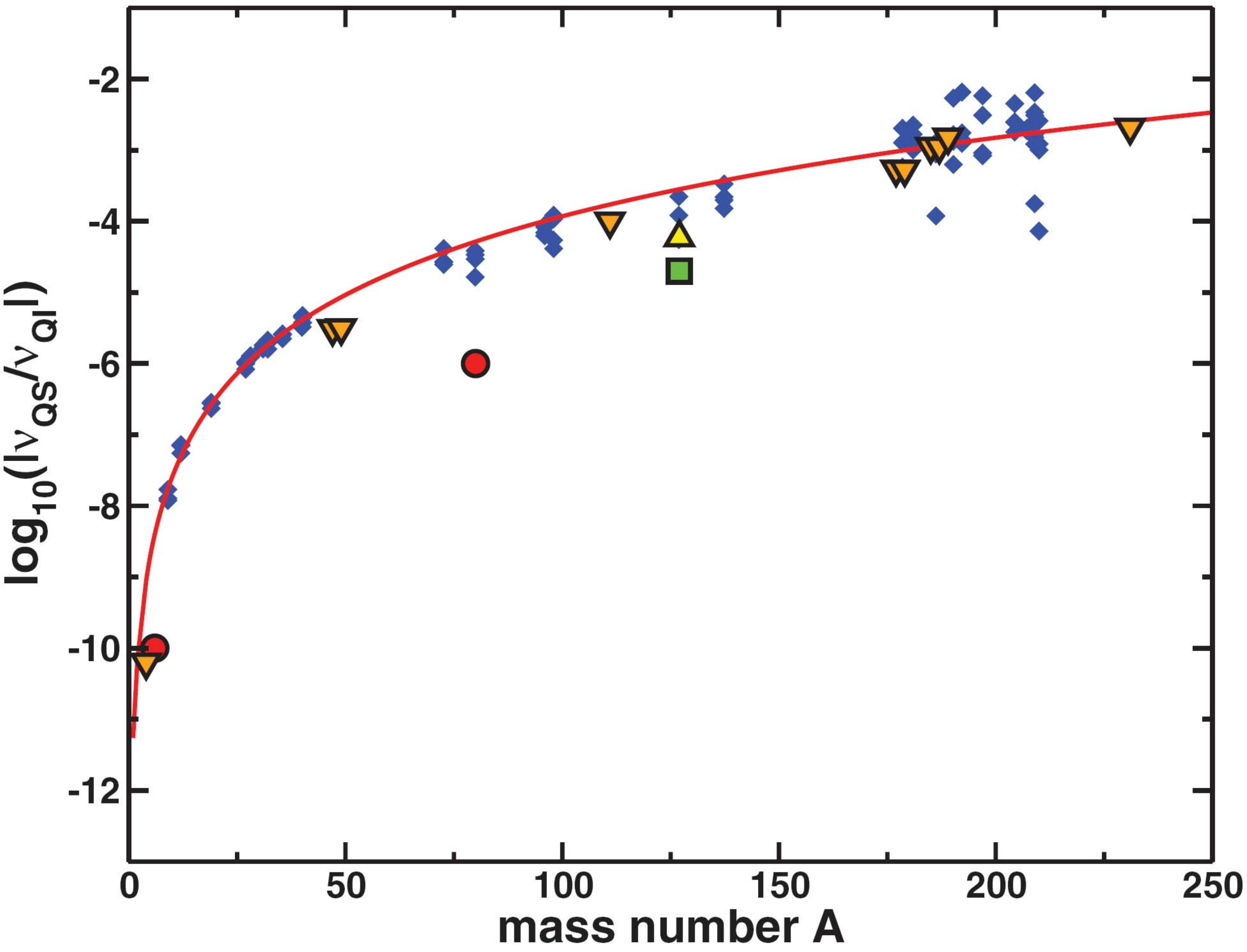
$$\nu_{\mathrm{QI}} = \frac{eQV_{zz}}{h}$$

new

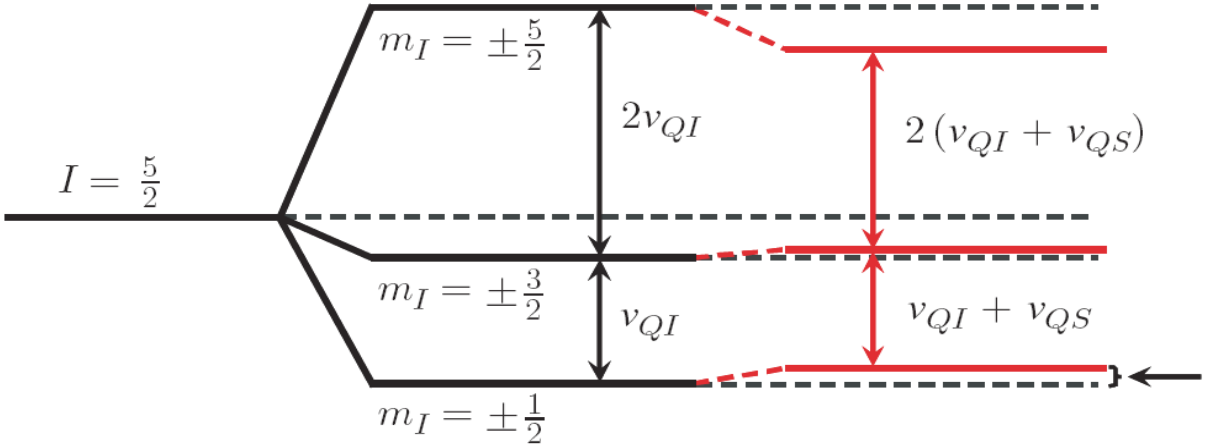
$$\nu_{\mathrm{QS}} = -\frac{e\tilde{Q}n_{zz}}{14\epsilon_0 h}$$



Quadrupole Interaction + **Quadrupole Shift**

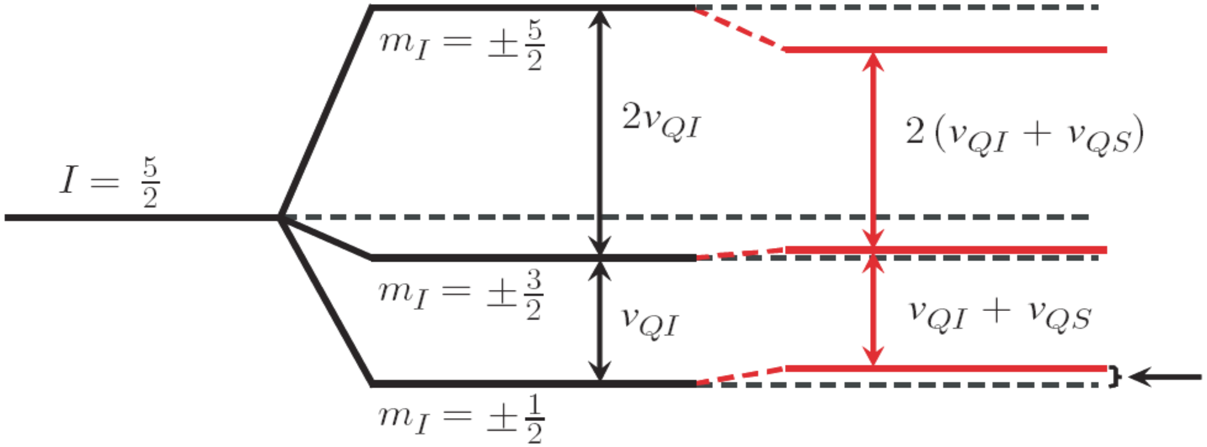


calculations done by FPLO code



Quadrupole Interaction + **Quadrupole Shift**

isotope shift	compare two isotopes
isomer shift	compare source and absorber
Bohr-Weisskopf effect (hyperfine anomaly)	compare μ-ratio with and without field



Quadrupole Interaction + **Quadrupole Shift**

isotope shift	compare two isotopes
isomer shift	compare source and absorber
Bohr-Weisskopf effect (hyperfine anomaly)	compare μ-ratio with and without field
quadrupole anomaly	compare Q-ratio from 4 measurements

The first quadrupole anomaly experiment has been performed !

David Dewald & Jens-Uwe Grabow
Gottfried-Wilhelm-Leibniz-Universität, Hannover

High-precision quadrupole interaction experiments in a set of 4 suitably chosen molecules (FTMW-spectroscopy).

$^{179}\mathrm{Hf}^{16}\mathrm{O}$	$^{177}\,\mathrm{Hf}^{16}\mathrm{O}$
$^{179}\mathrm{Hf}^{32}\mathrm{S}$	$^{177}\,\mathrm{Hf}^{32}\mathrm{S}$

quadrupole anomaly $\delta = 7(1) \cdot 10^{-6}$

Dewald & Grabow,
to be published

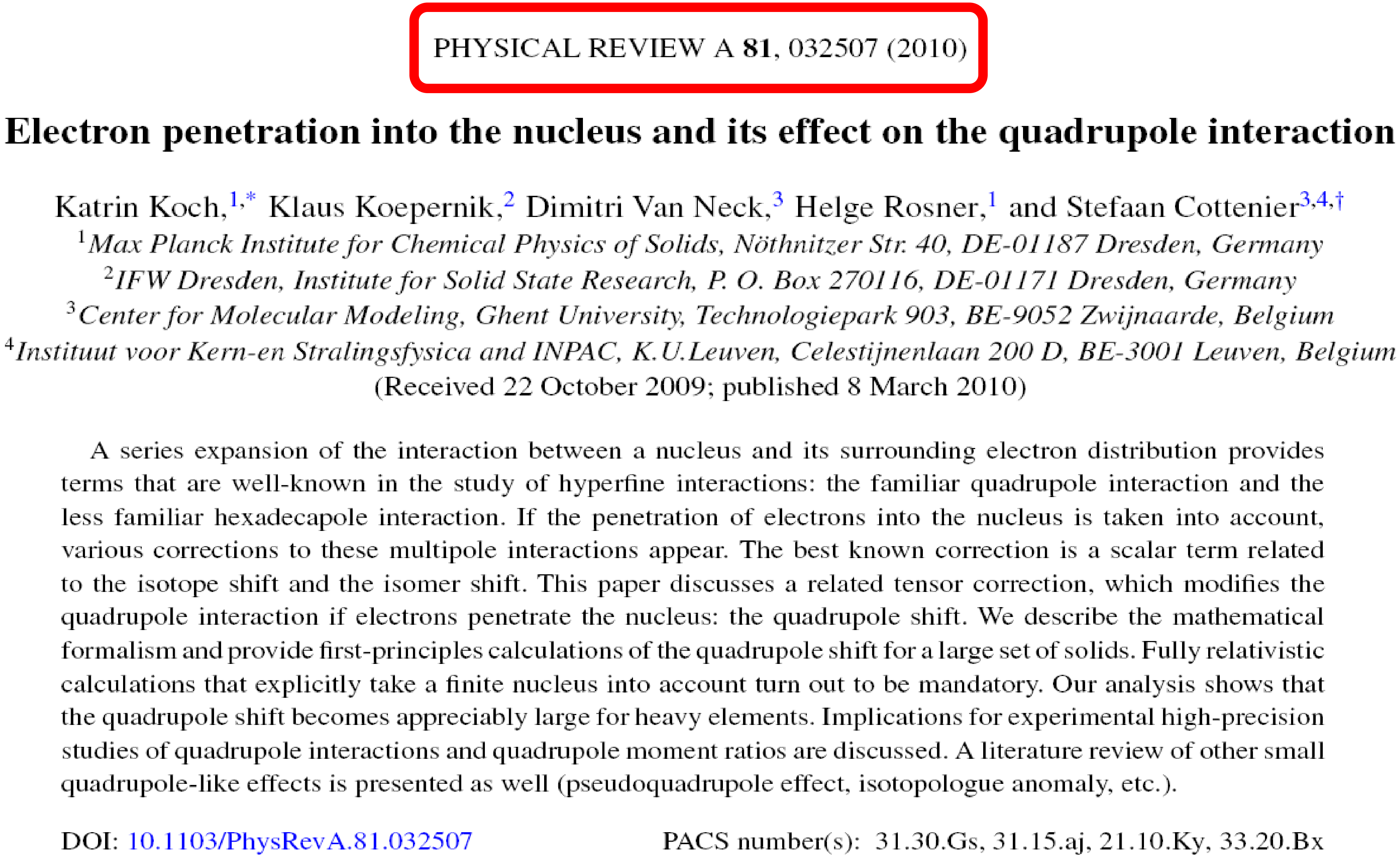
Conclusions

❶ We sketched the mathematical formalism for the quadrupole shift (QS).

❷ The QS is small: it is negligible for light elements, but for the heaviest elements it can be as large as 1%.

❸ The QS can be calculated from first principles. Fully relativistic calculations with a finite nucleus are required for this (➔ FPLO code).

❹ High-resolution molecular beam spectroscopy can observe the existence of the quadrupole shift through the quadrupole anomaly. A first experimental result is available now.



PHYSICAL REVIEW A **81**, 032507 (2010)

Electron penetration into the nucleus and its effect on the quadrupole interaction

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[2] *IFW Dresden, Institute for Solid State Research, P. O. Box 270116, DE-01171 Dresden, Germany*
[3] *Center for Molecular Modeling, Ghent University, Technologiepark 903, BE-9052 Zwijnaarde, Belgium*
[4] *Instituut voor Kern-en Stralingsfysica and INPAC, K.U.Leuven, Celestijnenlaan 200 D, BE-3001 Leuven, Belgium*

(Received 22 October 2009; published 8 March 2010)

A series expansion of the interaction between a nucleus and its surrounding electron distribution provides terms that are well-known in the study of hyperfine interactions: the familiar quadrupole interaction and the less familiar hexadecapole interaction. If the penetration of electrons into the nucleus is taken into account, various corrections to these multipole interactions appear. The best known correction is a scalar term related to the isotope shift and the isomer shift. This paper discusses a related tensor correction, which modifies the quadrupole interaction if electrons penetrate the nucleus: the quadrupole shift. We describe the mathematical formalism and provide first-principles calculations of the quadrupole shift for a large set of solids. Fully relativistic calculations that explicitly take a finite nucleus into account turn out to be mandatory. Our analysis shows that the quadrupole shift becomes appreciably large for heavy elements. Implications for experimental high-precision studies of quadrupole interactions and quadrupole moment ratios are discussed. A literature review of other small quadrupole-like effects is presented as well (pseudoquadrupole effect, isotopologue anomaly, etc.).

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