quantum multipole expansion

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- We did discuss the multipole expansion for a classical system
- We did discuss the perturbation theory method

➔ We will now discuss the multipole expansion for a quantum system. We will conclude it is identical to the classical case, except for the role of perturbation theory.

multipole expansion in quantum physics

1) Description of a free nucleus

$$\hat{H}_n = \hat{T}_n + \hat{U}_{nn}$$

$$\hat{H}_n \left| I \right\rangle = E_I \left| I \right\rangle$$

→ separated by keV/MeV

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multipole expansion in quantum physics

2) Description of a free electron cloud

$$\hat{H}_e = \hat{T}_e + \hat{U}_{ee}$$

$$\hat{H}_e \, |\psi_e\rangle = E_\psi \, |\psi_e\rangle$$

unbound

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multipole expansion in quantum physics

3) Description of nucleus that is NOT interacting with an electron cloud

$$\left(\hat{H}_n \otimes \mathbb{1} + \mathbb{1} \otimes \hat{H}_e\right) |I \otimes \psi_e\rangle = (E_I + E_\psi) \, |I \otimes \psi_e\rangle$$

(somewhat artificial, this is combining the two independent systems in one mathematical picture)

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multipole expansion in quantum physics

4) Description of a nucleus that is interacting with an electron cloud

Hamiltonian: $\hat{H}_n \otimes \mathbb{1} + \mathbb{1} \otimes \hat{H}_e + \hat{Q} \otimes \hat{V}$

It is the interaction term that makes life difficult. We can make a multipole expansion:

$$\hat{Q} \otimes \hat{V} = \hat{Q}^{(0)} \otimes \hat{V}^{(0)} + \hat{Q}^{(1)} \otimes \hat{V}^{(1)} + \hat{Q}^{(2)} \otimes \hat{V}^{(2)} + \dots$$

This leads to a hierarchy in energy scales (➔ perturbation theory will be convenient !) :

$\hat{T}_n \otimes \mathbb{1} + \hat{U}_{nn} \otimes \mathbb{1}$	$T_n + U_{nn}$	$keV - MeV$	*nuclear energy levels*
$\mathbb{1} \otimes \hat{T}_e + \mathbb{1} \otimes \hat{U}_{ee} + \hat{Q}^{(0)} \otimes \hat{V}^{(0)}$	$T_e + U_{ee} + E_{ne}^{(0)}$	$eV \ (meV)$	*atomic energy levels*
$\hat{Q}^{(1)} \otimes \hat{V}^{(1)} + \hat{Q}^{(2)} \otimes \hat{V}^{(2)}$	$E_{ne}^{(1)} + E_{ne}^{(2)}$	μeV	*hyperfine structure*

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multipole expansion in quantum physics

In the multipole-expanded formal hamiltonian, we will treat all nuclear properties as phenomenological parameters that are known (Z, I, Q, μ, <r²>,...)

The electronic properties will be kept as operators, and will have to be solved for.

$$\underbrace{\underbrace{\hat{H}_n \otimes 1\!\!1}_{\text{known}} + \underbrace{1\!\!1 \otimes \hat{H}_e + \hat{Q}^{(0)} \otimes \hat{V}^{(0)}}_{\text{the usual electron problem}}}_{\text{known}} + \underbrace{\hat{Q}^{(1)} \otimes \hat{V}^{(1)} +}_{\hat{H}_1}$$

known — the usual electron problem (you solved the hydrogen atom this way)

known

$\hat{H}_1$: small correction

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multipole expansion in quantum physics

Solution of the usual problem:

$$E_0 = \left\langle \psi_e^{(0)} \otimes I \middle| \hat{H}_0 \middle| I \otimes \psi_e^{(0)} \right\rangle$$

this wave function can be considered as known
(found by ab initio calculations for atoms, molecules or solids)

$$E_{tot} \approx E_0 + \left\langle \psi_e^{(0)} \otimes I \middle| \hat{H}_1 \middle| I \otimes \psi_e^{(0)} \right\rangle$$

known — known — known — known

energy corrections due to nuclear shape are computable ! (first order perturbation)

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multipole expansion in quantum physics
(charge-charge interaction)

⇨ The gravitational problem is fully equivalent to the quantum problem, except for the need to use perturbation theory.

Translation for the charge-charge interaction:

$$<\psi_n|\,\psi_n> = <I|\,I> = 1 = \int_n \psi_n^*(\boldsymbol{r}_n)\psi_n(\boldsymbol{r}_n)\,d\boldsymbol{r}_n = \frac{1}{Ze}\int_n \rho_n(\boldsymbol{r}_n)\,d\boldsymbol{r}_n$$

$$<\psi_e|\,\psi_e> = 1 = \int_e \psi_e^*(\boldsymbol{r}_e)\psi_e(\boldsymbol{r}_e)\,d\boldsymbol{r}_e = -\frac{1}{Ne}\int_e \rho_e(\boldsymbol{r}_e)\,d\boldsymbol{r}_e$$

$G \leftrightarrow \frac{-1}{4\pi\epsilon_0}$

$\boldsymbol{r}_1 \leftrightarrow \boldsymbol{r}_n$

$\boldsymbol{r}_2 \leftrightarrow \boldsymbol{r}_e$

$m_1 \leftrightarrow eZ$

$m_2 \leftrightarrow -eN$

⇨

$$E_{pot}^{qq} = \frac{1}{4\pi\epsilon_0}\int_n\int_e \frac{\rho_n(\boldsymbol{r}_n)\rho_e(\boldsymbol{r}_e)}{|\boldsymbol{r}_e - \boldsymbol{r}_n|}\,d\boldsymbol{r}_n\,d\boldsymbol{r}_e$$
$$= -\frac{e^2NZ}{4\pi\epsilon_0}\,\langle \psi_e \otimes I|\,\frac{1}{|\boldsymbol{r}_e - \boldsymbol{r}_n|}\,|I \otimes \psi_e\rangle$$

multipole expansion

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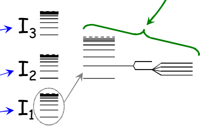
multipole expansion in quantum physics
(charge-charge interaction)

multipole expansion of the hamiltonian :

$$\hat{H}^{qq}_{ne} = -\frac{e^2 NZ}{\epsilon_0}\left(\sum_{n=0}^{\infty}\frac{r_n^n}{r_e^{n+1}}\frac{1}{2n+1}Y^n(\theta_n,\phi_n)\cdot Y^n(\theta_e,\phi_e)\right)$$

we assume here that electrons do not penetrate into the nucleus

$$E^{qq}_{tot} = \langle\psi_e\otimes I|\underbrace{\hat{T}_n+\hat{U}_{nn}}+\underbrace{\hat{T}_e+\hat{U}_{ee}+\hat{H}^{qq}_{ne}}|I\otimes\psi_e\rangle$$
$$= (E_I + E_{el})\,|I\otimes\psi_e\rangle$$



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multipole expansion in quantum physics
(charge-charge interaction)

$$E_{el} = \langle\psi_e\otimes I|\underbrace{\hat{T}_e+\hat{U}_{ee}-\frac{e^2NZ}{4\pi\epsilon_0\, r_e}}_{\hat{H}_0}|I\otimes\psi_e\rangle\ +$$
$$\langle\psi_e\otimes I|\underbrace{-\frac{e^2NZ}{\epsilon_0}\left(\sum_{n=1}^{\infty}\frac{r_n^n}{r_e^{n+1}}\frac{1}{2n+1}Y^n(\theta_n,\phi_n)\cdot Y^n(\theta_e,\phi_e)\right)}_{\hat{H}_{1\to\infty}}|I\otimes\psi_e\rangle$$

$$Q^n_q = eZ\sqrt{\frac{4\pi}{2n+1}}\,\langle I|\,r_1^n Y_q^n(\theta_n,\phi_n)\,|I\rangle$$

nuclear multipole moments
(lousely computable in ab initio nuclear physics theory – we take it as a (experimentally) given object)

$$V^n_q = -\frac{eN}{\sqrt{4\pi\epsilon_0}}\sqrt{\frac{1}{2n+1}}\left\langle\psi_e^{(0)}\middle|\frac{1}{r_e^{n+1}}Y_q^n(\theta_e,\phi_e)\middle|\psi_e^{(0)}\right\rangle$$

electric multipole fields
(reasonably well computable in ab initio “electron” theory [=atoms, molecules, solids])

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multipole expansion in quantum physics
(charge-charge interaction)

$$H \approx \hat{T}_n+\hat{U}_{nn}+\underbrace{\hat{T}_e+\hat{U}_{ee}-\frac{e^2NZ}{4\pi\epsilon_0\, r_e}}_{\hat{H}_0}+\underbrace{\frac{-e^2NZ}{5\epsilon_0}\left(\frac{r_n^2}{r_e^3}Y^2(\theta_e,\phi_e)\cdot Y^2(\theta_n,\phi_n)\right)}_{\hat{H}_1}$$

- odd terms vanish
- truncate after quadrupole term

$$E_{tot} \approx E_0 + \left\langle\psi_e^{(0)}\otimes I\middle|\hat{H}_1\middle|I\otimes\psi_e^{(0)}\right\rangle$$

known, known, known, known

known

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multipole expansion in quantum physics
(current-current interaction)

Vector potential due to a given current distribution: $\boldsymbol{A}(\boldsymbol{r}) = \frac{\mu_0}{4\pi} \int \frac{\boldsymbol{j}(\boldsymbol{r}')}{|\boldsymbol{r}' - \boldsymbol{r}|} \, d\boldsymbol{r}'$

Energy for the interaction between two current distributions :

$$E^{jj}_{pot} = \int_n \boldsymbol{j}_n(\boldsymbol{r}_n) \cdot \boldsymbol{A}_e(\boldsymbol{r}_n) \, d\boldsymbol{r}_n = \frac{\mu_0}{4\pi} \int_n \int_e \frac{\boldsymbol{j}_n(\boldsymbol{r}_n) \cdot \boldsymbol{j}_e(\boldsymbol{r}_e)}{|\boldsymbol{r}_e - \boldsymbol{r}_n|} \, d\boldsymbol{r}_n \, d\boldsymbol{r}_e$$

Multipole expansion (different mathematics due to vector quantities) :

$$\hat{H}_{jj} = \sum_{n=0}^{\infty} \frac{B^{(n)} \cdot M^{(n)}}{2n+1}$$

- nuclear magnetic multipole moments
- magnetic multipole fields

Even terms vanish – dipole term is the leading one :

dipole hamiltonian: $-\hat{\boldsymbol{\mu}}_I \cdot \hat{\boldsymbol{B}}(\boldsymbol{0})$

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multipole expansion in quantum physics
(summary / overview)

We want to have the energy corrections due to H_1, with and without overlap :

$$\hat{H} \approx \underbrace{\hat{T}_n + \hat{U}_{nn} + \hat{T}_e + \hat{U}_{ee} - \frac{e^2 N Z}{4\pi\epsilon_0 \, r_e}}_{\hat{H}_0} + \underbrace{\frac{-e^2 N Z}{5\epsilon_0} \left(\frac{r_n^2}{r_e^3} Y^2(\theta_e, \phi_e) \cdot Y^2(\theta_n, \phi_n) \right) - \hat{\boldsymbol{\mu}}_I \cdot \hat{\boldsymbol{B}}(\boldsymbol{0})}_{\hat{H}_1}$$

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multipole expansion in quantum physics
(summary / overview)

Fig. 3.1	monopole	dipole	quadrupole	octupole
charge-charge (no overlap)	"normal" electronic structure [a] Q V(0)		electric-field gradient [b] $Q^{(2)} \cdot V^{(2)}(0)$	
charge-charge (overlap)	isotope shift isomer shift [d]		(too small) [e]	
current-current (no overlap)		orbital field spin dipolar field $\vec{\mu}_I \cdot \vec{B}_{hf}$		(too small)
current-current (overlap)		Fermi contact field $\vec{\mu}_I \cdot \vec{B}_{hf}$ / Bohr-Weisskopf		(too small)

Fig. 3.1. *A schematic overview of all contributions to electric (charge-charge) and magnetic (current-current) hyperfine fields, ordered according to their multipole order, and split into shape-dependent and size-dependent contribution. Contributions that do not exist are barred, contributions that are too small to be relevant are indicated. When a dashed line is present in a box, the contribution above the line does not vanish for a point nucleus, while the contribution below the line does. Explaining this scheme is the task of chapters 4 to 7.*

(the letters in square brackets refer to the next page).

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multipole expansion in quantum physics

(summary / overview)

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]	$\tilde{M}^{(1)} \propto \{r^2 Y_{00}\}$, $\tilde{V}^{(1)} \propto \Delta v(0)$ } MS$^{(1)}$ [d]	$\tilde{M}^{(2)} \propto \{r^4 Y_{00}\}$, $\tilde{V}^{(2)} \propto \Delta^2 v(0)$ } MS$^{(2)}$	...
$\mathcal{O}(2)$	$Q \propto r^2 Y_{20}$, $V_{ij} \propto \partial_{ij} v(0)$ } QI [b]	$\tilde{Q}^{(1)} \propto \{r^4 Y_{20}\}$, $\tilde{V}_{ij}^{(1)} \propto \partial_{ij} \Delta v(0)$ } QS$^{(1)}$ [e]	$\tilde{Q}^{(2)} \propto \{r^6 Y_{20}\}$, $\tilde{V}_{ij}^{(2)} \propto \partial_{ij} \Delta^2 v(0)$ } QS$^{(2)}$	...
$\mathcal{O}(4)$	$H \propto r^4 Y_{40}$, $V_{ijkl} \propto \partial_{ijkl} v(0)$ } HDI [c]	$\tilde{H}^{(1)} \propto \{r^6 Y_{40}\}$, $\tilde{V}_{ijkl}^{(1)} \propto \partial_{ijkl} \Delta v(0)$ } HDS$^{(1)}$	$\tilde{H}^{(2)} \propto \{r^8 Y_{40}\}$, $\tilde{V}_{ijkl}^{(2)} \propto \partial_{ijkl} \Delta^2 v(0)$ } HDS$^{(2)}$	...
...	...	...	...	...

- multipole interaction
- first order multipole shift
- second order multipole shift
- ...

Table 1. Systematic overview of nuclear multipole and quasi multipole moments and electronic multipole and quasi multipole fields that appear in the multipole expansion of for two interacting (and overlapping) classical charge distributions. The first column gives the regular multipole expansion for point nuclei: the monopole interaction (labeled by [a]) which provides the unperturbed hamiltonian in a quantum frame-work. This is perturbed by [b] the quadrupole and [c] the hexadecapole interaction. The next columns give the quasi multipole moments/fields for every multipole interaction, denoted by a tilde. They provide first order corrections (shifts) to the multipole interactions of the first column, due to the extendedness of the nucleus. The box labeled [d] gives rise to the isomer/isotope shift, while the box labeled by [e] is the main topic of the present paper. Colored (gray) text is by extrapolation only, and is not systematically derived in this paper. The objects in each line are spherical tensors of a given rank (rank 0 for line 1, rank 2 for line 2, rank 4 for line 3, ...).

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summary

The quantum case is as the classical (gravitation) case,
apart from perturbation theory.

We have a roadmap of the kind of interactions we have to study.

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