

The mean-field approximation

$$H = \sum_i \left(-\frac{\hbar^2}{2m} \nabla_i^2 - \frac{Ze^2}{4\pi\epsilon_0 r_i} \right) + \sum_{ij} \frac{e^2}{4\pi\epsilon_0 r_{ij}}$$

We expect that the $\frac{Ze^2}{4\pi\epsilon_0 r_i}$ terms are

strongly reduced by the $\frac{e^2}{4\pi\epsilon_0 r_{ij}}$ because of the

screening of the nucleus by the other $N-1$ electrons.

rewrite the Hamiltonian as:

$$H = H_0 + H_1$$

$$H_0 = \sum_i \left(-\frac{\hbar^2}{2m} \nabla_i^2 + U(r_i) \right)$$

$$H_1 = \sum_{ij} \frac{e^2}{4\pi\epsilon_0 r_{ij}} - \sum_i \left(\frac{Ze^2}{4\pi\epsilon_0 r_i} + U(r_i) \right)$$

we hope that $H_1 \ll H_0$, and the electron-electron interaction is described by a mean-field potential $U(r_i)$.

now neglect H_i , and we must solve

$$H_0 \Psi = \sum_i \left(\frac{\hbar^2}{2m} \nabla_i^2 + U(r_i) \right) \Psi = E \Psi$$

since this H only has single particle terms ($H = \sum h_i$)

$$\Psi = \prod_i \psi_i$$

$$\text{and } E = \sum_i E_{n_i l_i m_i}$$

for each electron

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + U(r) \right) \Psi_{n_l m_l m_s} = E_{n_l m_l m_s} \Psi_{n_l m_l m_s}$$

- we have assumed U is a central potential (depends only on r).

then just like solving the H atom

$$\Psi_{n_l m_l m_s} = R_{n_l}(r) Y_L^m(\theta, \phi) \chi(m_s)$$

- the problem is solving for R_{n_l} in this potential whose form depends on the distribution of electrons, which depends on the soln. of R_{n_l} . . .

use an iterative approach.

A. guess a form for $U(r_k)$

(e.g. use shielded Coulomb potnl.)

B. solve (numerically) for all $\psi_{n\ell}$.

C. improve $U(r_k)$:

$$U(r_k) = \frac{-Ze^2}{4\pi\epsilon_0 r_k} + \left\langle \sum_{i \neq k} \int \frac{e^2}{4\pi\epsilon_0 r_{ik}} (e^{-q_i^* q_i}) dr_i \right\rangle$$

↳ average over angles so
that U stays central

D. go to step B and iterate until convergence
to self-consistent $U(r_k)$; ψ_k 's.

this method (Hartree) produces a wave fn.

$$\Psi = \prod_k \psi_k \quad \text{which is not properly symmetrized}$$

If instead we use Slater determinants for the ψ_k 's,
it is called the Hartree-Fock method, and
results in proper antisymmetric wave fns.

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An approximation of the central potential

- the Thomas-Fermi model

model the atom as a $T=0$ Fermi gas in a potential.

$$\frac{N}{V} = \frac{2}{h^3} \frac{4\pi \hbar^3 k_F^3}{3} \underbrace{\text{volume of sphere in mom. space}}_{\text{volume of phase space element}}$$

$$\frac{N}{V} = \frac{8\pi}{3h^3} (2mT_0)^{3/2} \quad (T_0 = \frac{\hbar^3 k_F^2}{2m})$$

$$T_0 = \text{max. kinetic energy} = e\phi(r_0)$$

$$\rho = \frac{eN}{V} = -\frac{8\pi}{3h^3} e(2me\phi)^{3/2}$$

$$\text{Poisson's eq. } \nabla^2 \phi = -\rho/\epsilon_0$$

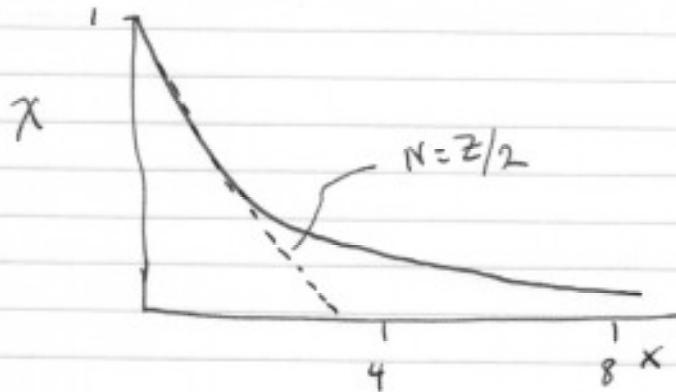
$$\Rightarrow \nabla^2 \phi = \frac{4}{3\pi h^3} \frac{e(2me\phi)^{3/2}}{4\pi\epsilon_0}$$

$$\text{assume } \phi(r) = X(r) \frac{ze}{4\pi\epsilon_0 r}$$

end up with diff. eq.

$$\frac{d^2 X}{dx^2} = x^{-1/2} X^{3/2}$$

$$X = (3\pi)^{-2/3} 2^{7/3} \frac{me^2}{4\pi\epsilon_0 \hbar^2} z^{1/3}$$



$$U(r) = -\frac{Ze^2}{r} \chi\left(\frac{r}{b}\right) \quad \text{for } N=Z$$

- a useful trial potential for Hartree-Fock or other methods
- actually does a good job of telling at what Z an electron with n, l will be bound, if we include centrifugal potential

$$U'(r) = U(r) + \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2}$$

$$\Rightarrow \text{gives } Z = 5, 21, 58, 124$$

for $l=1, 2, 3, 4$

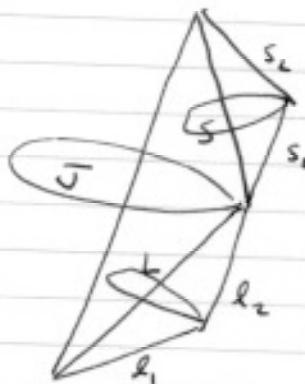
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Fine Structure

The spin-orbit interaction is

$$H_{so} = V_{so} \vec{L} \cdot \vec{S}$$

$$\text{where } \vec{L} = \sum_i l_i, \quad \vec{S} = \sum_i \vec{s}_i$$



$$\vec{L} + \vec{S} = \vec{J}$$

then $\Delta E_{FS}^{(1)} = \langle L S M_L M_S | \frac{e^2}{4\pi\epsilon_0 r_{ij}} | L S M_L M_S \rangle$

represents the shift in energy associated with the electron-electron interactions. This will potentially lift degeneracy, but we are still assuming L : S are good quantum numbers.

the spin-orbit term mixes $L \cdot \vec{S}$

define new basis fns.

$$\Psi(R, LSJM_J) = \sum_{M_L} C(LSJ; M_L, M_S - L) \Psi(R, LSJ)$$

then the energy shift will be

$$\Delta E_{FS}^{(2)} = \langle LSJM_J | \vec{\psi}_0 \vec{L} \cdot \vec{S} | LSJM_J \rangle$$

$$= \langle LSJM_J | \mathcal{G}(L, S) \{ J(J+1) - L(L+1) - S(S+1) \} | LSJM_J \rangle$$

\mathcal{G} ~ dimensions of energy, const. within a term

- produces a multiplet of ~closely spaced levels

- each level is still $2J+1$ degenerate.

- note if $S=0$, $J=L$; $\Delta E_{FS}^{(2)} = 0$

- within a multiplet

$$\Delta E_{FS}^{(2)}(J) - \Delta E_{FS}^{(2)}(J-1) = J$$

"Lande' interval rule"

Hypertine structure

- nucleus may have spin \vec{I} , mag. moment $\vec{\mu}_I$

Pauli 1924: explained some structure in spectra

$$H' = -\vec{\mu}_I \cdot \vec{B}_{el}(0) \quad \text{contact approximation}$$

- write $\vec{\mu}_I = g_I \mu_N \vec{I}$

where $\mu_N/\mu_B \sim 1/2000$

since $\vec{B}_{el}(0)$ comes from motion of the atoms, can write

$$H' = A_J \vec{I} \cdot \vec{J}$$

A_J = magnetic hyperfine structure constant

- a nucleus also has a finite extent (not quite a point particle)

consider

$$H'' = -\frac{e^2}{4\pi\epsilon_0 |\vec{r}_e - \vec{r}_n|}$$

can write as

$$\mathcal{H}'' = \frac{-e^2}{4\pi\epsilon_0} \sum_k \frac{r_n^{-k}}{r_e^{k+1}} P_k(\cos\theta_{en})$$

$k=0$ corresponds to monopole term

$$e^2/4\pi\epsilon_0 r$$

$k=1$ corresponds to nuclear electric dipole
which must be zero if T-reversal is good symmetry.

using spherical harmonic addition th..

$$P_k(\cos\theta_{en}) = \frac{4\pi}{2k+1} \sum_{g=-k}^k (-1)^g Y_k^g(\theta_n, \phi_n) Y_k^g(\theta_e, \phi_e)$$

we can write $k=2$ term as

$$\mathcal{H}_2'' = \frac{1}{4\pi\epsilon_0} \sum_{g=-2}^2 (-1)^g \left\{ \left(\frac{4\pi}{5}\right)^{1/2} e r_n^{-2} Y_2^{-g}(\theta_n, \phi_n) \right\} \\ \left\{ \left(\frac{4\pi}{5}\right)^{1/2} \left(\frac{-e}{r_e^3}\right) Y_2^g(\theta_e, \phi_e) \right\}$$

$$= \frac{1}{4\pi\epsilon_0} \sum_g (-1)^g Q_2^g(n) F_e^g(e)$$

nuclear quadrupole tensor

electric field gradient

define a nuclear quadrupole moment:

$$\begin{aligned} Q &= \frac{e}{c} \left\langle I, M_I = I \right| \sum_j Q_2^0(n_j) \left| I, M_I = I \right\rangle \\ &= \left\langle II \right| \sum_j r_{n_j}^2 (3 \cos^2 \Theta_{n_j} - 1) \left| II \right\rangle \\ &\quad \text{sum over protons in nucleus} \end{aligned}$$

define average field gradient at nucleus

$$\begin{aligned} \left\langle \frac{\partial^2 V_e}{\partial z^2} \right\rangle &= \frac{2}{4\pi\epsilon_0} \left\langle JJ \right| \sum_i F_2^0(e_i) \left| JJ \right\rangle \\ &= - \left\langle JJ \right| \sum_i \frac{e(3 \cos^2 \Theta_{e_i} - 1)}{4\pi\epsilon_0 r_{e_i}^3} \left| JJ \right\rangle \end{aligned}$$

then one can show

$$H_2'' = \frac{B_J}{2I(2I-1)J(2J-1)} \left\{ 3(\vec{I} \cdot \vec{J})^2 + \frac{3}{2}(\vec{I} \cdot \vec{J}) - I(I+1)J(J+1) \right\}$$

$$\text{where } B_J = eQ \left\langle \frac{\partial^2 V_e}{\partial z^2} \right\rangle$$

is the electric quadrupole hyperfine constant

note need $I > J$ to have non-zero Q

now we can couple nuclear spin with electronic ang. momentum to yield a total angular momentum

$$\vec{F} = \vec{I} + \vec{J}$$

energy levels:

$$E_F = \langle \gamma J I F M_F | H_b + H_{hf} | \gamma J I F M_F \rangle$$

$$= E_J + \frac{1}{2} A_J K + \frac{B_J}{8I(2I+1)J(2J+1)} \{ 3K(K+1) - 4I(I+1)J(J+1) \}$$

$$\text{where } K = F(F+1) - I(I+1) - J(J+1)$$

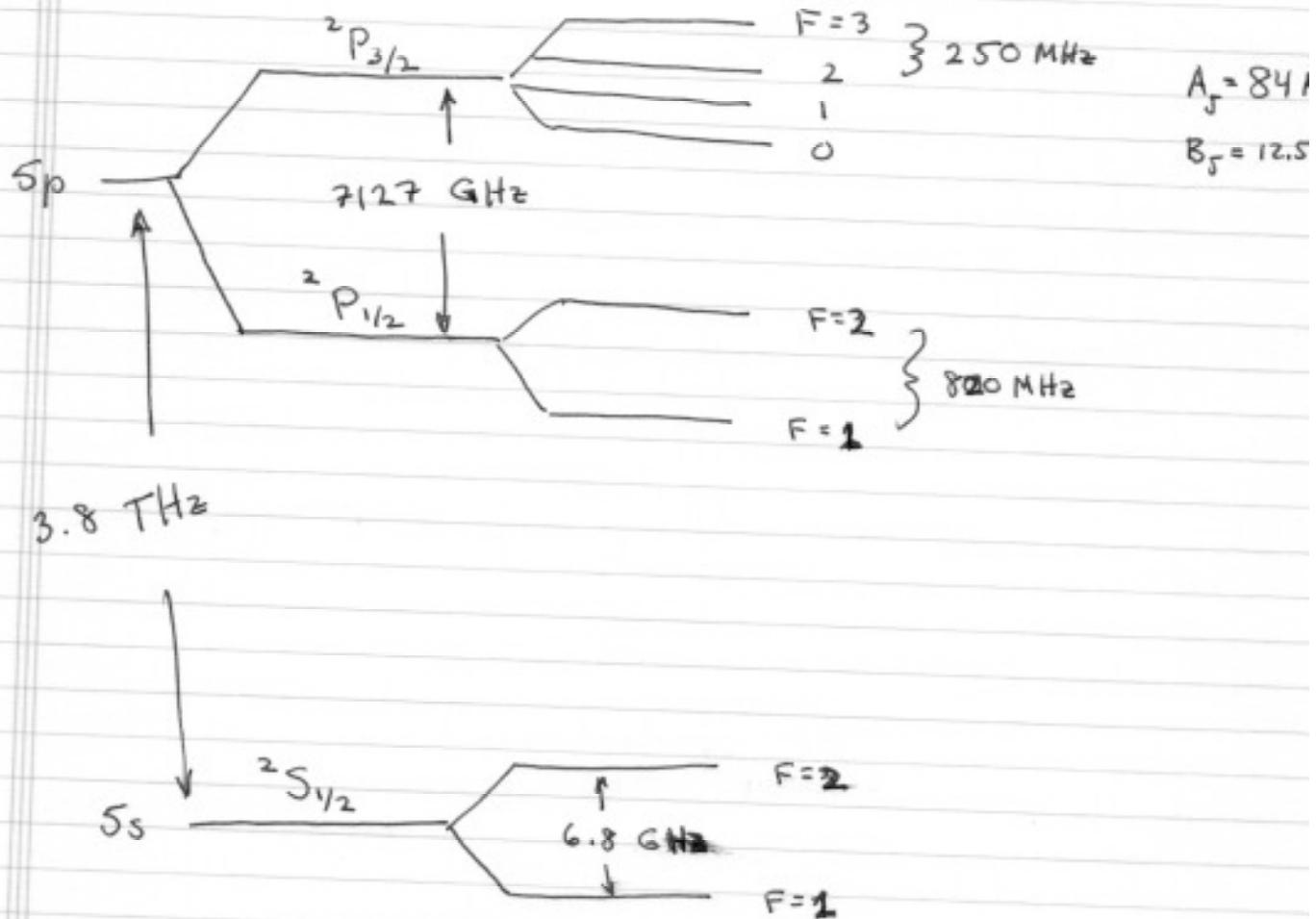
- states will be $2F+1$ degenerate

note if $B_J \ll A_J$ $4E_F - E_{F-1} = A_J F$

(a hyperfine version of
the Lande' interval rule).

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~ an example

 ^{87}Rb $I = \frac{3}{2}$ 

Multipole expansion:

total H for atom + field

$$H = \frac{1}{2m} \sum_j (\hat{p}_j + e\hat{A}(\vec{r}_j))^2 + \frac{1}{2} \int \sigma(\vec{r}) \phi(\vec{r}) d\vec{r} + \frac{1}{2} \int \epsilon_0 \hat{E}_T^2 + \frac{1}{\mu_0} \hat{B}^2 d\vec{r}$$

\hat{p}_j = momentum of electron j

\vec{r}_j = position

$\sigma(\vec{r})$ = charge distribution

$\phi(r)$ = scalar potential

\hat{E}_T = transverse field

- 2nd term is electrostatic energy
- 3rd term is EM field energy

expanding the 1st term

$$\frac{1}{2m} \sum \hat{p}_j^2 + \frac{e}{2m} \sum \hat{A} \cdot \hat{p} + \frac{e^2}{2m} \sum A^2$$

↑
Kinetic

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atom-field interaction

(?)

if we assume the field is not too strong  
we can expect  $\vec{p} \cdot \vec{A} \gg A^2$

$A^2 \sim 2\text{-photon processes}$  (recall  $A$  in terms  
of  $a_k^\dagger, a_k$ )

so atom-field interaction  $\sim \vec{p} \cdot \vec{A}$

in electric dipole approximation

$$e^{ik \cdot \vec{r}} \approx 1 + ik \cdot \vec{r} + \frac{1}{2} (ik \cdot \vec{r})^2 + \dots$$

$$\approx 1 + f \quad (\text{dipole approximation})$$

one can show

$$\vec{p} \cdot \vec{A} \rightarrow \vec{d} \cdot \vec{E}$$

Electric dipole E1

- if we look at  $ik \cdot \vec{r}$ , this corresponds  
to the magnetic dipole & electric  
quadrupole terms.

Classical (see Jackson) radiated power  
of oscillating magnetic dipole:

$$P_{M1} = \frac{\mu_0 k^4 c}{12\pi} |\vec{\mu}|^2$$

as with electric dipoles,

$$A_{M1} = \frac{\mu_0 \omega^3}{3\pi \hbar c^3} \frac{1}{g_k} \sum_{m_k m_i} |\langle k \omega_k | \vec{\mu} | i m_i \rangle|^2$$

$$\text{where } \vec{\mu} = -\mu_B (\vec{L} + \vec{S})$$

recalling our result for <sup>electric</sup><sub>dipole</sub> radiation,  
we find

$$\frac{A_{M1}}{A_{E1}} \sim \frac{1}{c^2} \left| \frac{\mu}{e r} \right|^2 \sim \left[ \frac{2 \mu_B}{e a_0 c} \right]^2 = \left[ \frac{2 \alpha}{2} \right]^2$$

~ typically  $10^{-5}$

if  $A_{E1} \sim 10^8 \text{ s}^{-1}$  ( $\tau \sim 10 \text{ ns}$ )

$A_{M1} \sim 10^3 \text{ s}^{-1}$  ( $\tau \sim \text{ms}$ )

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A similar story for electric quadrupole:

$$A_{E2} = \frac{\omega^5}{360\pi\varepsilon_0\hbar c^5} \sum_{m_k m_i} \left| \langle k m_k | -e \sum_i 3\vec{r}_i \vec{r}_i - \vec{r}_{i\alpha}^2 \rangle_i \right|^2$$

where  $\vec{r}_i$  are Cartesian components of  $\vec{r}$

quadrupole operator  $\hat{Q} = -e \sum_i (3\vec{r}_i \vec{r}_i - \vec{r}_i^2) \hat{L}_i$   
identical tensor

one finds

$$\frac{A_{E2}}{A_{E1}} \sim \frac{3}{40} \left( \frac{\omega r}{c} \right)^2 \sim \frac{3}{40} \left[ \frac{2\alpha}{2} \right]^2 \sim 10^{-6}$$

$$\tau_{E2} \sim 10 \text{ ms}$$

By looking at the symmetries of the various multipole operators, one can develop a set of selection rules for single-photon transitions

## Selection Rules

electric dipole  
E1magnetic dipole  
M1elec. quadrupole  
E2

1)  $\Delta J = 0, \pm 1$

$0 \leftrightarrow 0$

$\Delta J = 0, \pm 1$

$0 \leftrightarrow 0$

$\Delta J = 0, \pm 1, \pm 2$

$0 \leftrightarrow 0, \frac{1}{2} \leftrightarrow \frac{1}{2}, 0 \leftrightarrow$

2)  $\Delta M = 0, \pm 1$

$\Delta M = 0, \pm 1$

$\Delta M = 0, \pm 1, \pm 2$

3) parity change  
( $s \rightarrow p$ )

no parity change  
 $s \rightarrow d$

no parity ch  
 $s \rightarrow d$

(4) no  $e^-$  jump  
 $\Delta l = \pm 1$

no  $e^-$  jump  
 $\Delta l = 0, \Delta n = 0$

one or no  $e^-$  jump  
 $\Delta l = 0, \pm 2$

5)  $\Delta S = 0$

$\Delta S = 0$

$\Delta S = 0$

6)  $\Delta L = 0, \pm 1$   
 $0 \leftrightarrow 0$

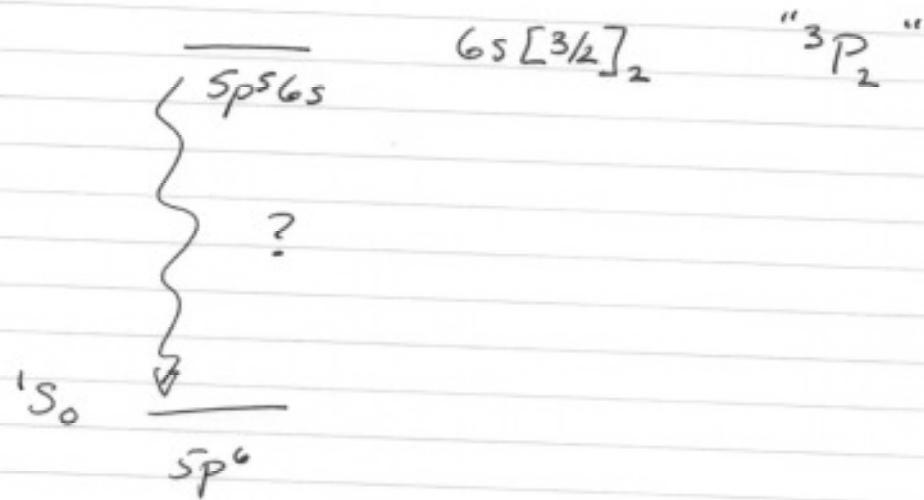
$\Delta L = 0$

$\Delta L = 0, \pm 1, \pm 2$   
 $0 \leftrightarrow 0, 0 \leftrightarrow 1$

→ approximate rules, maybe broken, especially  
for heavy atoms.

An example of a forbidden transition

Xe



have parity change ( $6s \rightarrow 5p$ )

- must be E1, E3, M2 ...

- have  $\Delta J = 2$

- lowest order transition is M2

magnetic quadrupole

$$\uparrow_{6s[3/2]_2} = 43 \text{ seconds!}$$

M. Walhout, et al.  
PRL 72, 2843 (94)

(if E1 would be  $\sim 1 \text{ ns!}$ )

note: if ...

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If states are high forbidden for single-photon processes, we must consider 2-photon transition.

- M. Göppert - Mayer 1931 (PhD thesis)

$$A_{2E_1}(\omega) d\omega = \frac{8e^4}{(4\pi\epsilon_0)^2 \pi \hbar^2 c^6} \omega_1^3 \omega_2^3 |\overline{M}_{ikl}|^2 d\omega,$$

where  $\hbar\omega_1 + \hbar\omega_2 = \hbar\omega_{ki}$

and  $M_{ik} = \sum_j \left\{ \frac{\langle i | \hat{\epsilon}_i \cdot \vec{r} | j \rangle \langle j | \hat{\epsilon}_i \cdot \vec{r} | k \rangle}{\omega_2 + \omega_{jk}} + \frac{\langle i | \hat{\epsilon}_i \cdot \vec{r} | j \rangle \langle j | \hat{\epsilon}_i \cdot \vec{r} | k \rangle}{\omega_1 + \omega_{jk}} \right\}$

$\hat{\epsilon}_i$  polarization of emitted photons

$|\overline{M}_{ikl}|$  denotes average over  $k \in \hat{\epsilon}_i$

