# Calculation of hyperfine field in WIEN2k

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## I. GENERAL SCHEME

Hyperfine field on a nuclei of an atom may be written as

$$B_{hf} = B_c + B_{dip} + B_{orb} + B_{lat}, \tag{1}$$

where $B_c$ is the Fermi contact term, $B_{dip}$ is the dipolar field from the on-site spin density, $B_{orb}$ is the field associated with the on-site orbital moment. $B_{lat}$ is classical dipolar field from all other atoms in the system that carry the magnetic moment and its calculation is described in detail in [1]. Calculation of $B_c$ is performed in standard spin-polarized WIEN2k calculation. Below we compare the calculation of $B_c$, $B_{dip}$ and $B_{orb}$ as described in the book of Abragam and Bleaney [2] (denoted in what follows as $\mathcal{A}$) and in the paper by Blügel *et al.* [3] ($\mathcal{B}$).

### A. $B_{hf}$ of Abragam and Bleaney

The interaction of nuclear spin $\vec{I}$ located at $\vec{r} = 0$ with electron spin $\vec{s}$ and orbital moment $\vec{l}$ is given by eq. ($\mathcal{A}$ 17.30):

$$H_n = 2\mu_B\, \gamma_n\, \hbar\, \vec{I} \left[ \frac{\vec{l}}{r^3} - \frac{\vec{s}}{r^3} + 3\frac{\vec{r}\,(\vec{s}\,\vec{r})}{r^5} + \frac{8}{3}\pi\, \vec{s}\, \delta(\vec{r}) \right]. \tag{2}$$

The nuclear magnetic moment $\vec{\mu}_I$ is ($\mathcal{A}$, 1.18-1.19)

$$\vec{\mu}_I = \gamma_n\, \hbar\, \vec{I}. \tag{3}$$

First term in (2) corresponds to interaction with the orbital moment, second and third term correspond to iteraction with the electron spin and the last term is the contact interaction.

Energy of the nuclear magnetic moment in the magnetic field $\vec{B}_{ext}$ is ($\mathcal{A}$, 1.27)

$$W_{ext} = -\vec{\mu}_I\, \vec{B}_{ext}. \tag{4}$$

By comparison of (2) and (4) we get for the orbital, spin dipolar and contact hyperfine fields the expressions:

$$\vec{B}_{orb} = -2\mu_B\, \frac{\vec{l}}{r^3}, \tag{5}$$

$$\vec{B}_{dip} = -2\mu_B \left[ 3\, \frac{\vec{r}\,(\vec{s}\,\vec{r})}{r^5} - \frac{\vec{s}}{r^3} \right], \tag{6}$$

and

$$\vec{B}_c = -2\mu_B\, \frac{8}{3}\pi\, \vec{s}\, \delta(\vec{r}) \tag{7}$$

$B_c$ is therefore opposite to the spin density at the nucleus.

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### B. $B_{hf}$ of Blügel et al.

The energy of the interaction of nuclear spin with the orbital moment $\vec{l}$ of an electron localized on atom in question (contrary to $\mathcal{A}$ $\vec{l}$ is in units of $\hbar$) is ($\mathcal{B}$, eq.24)

$$E_{orb} = -\frac{e}{mc}\vec{\mu}_I \,\langle\Phi|\frac{S(r)}{r^3}\vec{l}\,|\Phi\rangle \tag{8}$$

where $\Phi$ is the large component of the relativistic wave function, $m$ is the electron mass, $S(r)$ is reciprocal of the relativistic mass enhancement ($\mathcal{B}$, eq.21):

$$S(r) = \left[1 + \frac{\epsilon - V(r)}{2mc^2}\right]^{-1}. \tag{9}$$

The energy of dipolar interaction of nuclear spin with the electron spin magnetic moment $\vec{\mu}$ is ($\mathcal{B}$, eq.26)

$$E_{dip} = \langle\Phi|\frac{S(r)}{r^3}[\vec{\mu}\,\vec{\mu}_I - 3(\vec{\mu}\,\hat{\vec{r}})(\vec{\mu}_I\,\hat{\vec{r}})]|\Phi\rangle;\quad \hat{\vec{r}} = \vec{r}/r. \tag{10}$$

We now use that $\mu_B = e\hbar/2mc$ and $\vec{\mu} = 2\mu_B\vec{s}$, $\vec{s}$ being the electron spin. Eqs. (11, 12) then reduce to:

$$E_{orb} = -2\vec{\mu}_I\,\mu_B\langle\Phi|\frac{S(r)}{r^3}\vec{l}\,|\Phi\rangle \tag{11}$$

$$E_{dip} = 2\mu_B\,\vec{\mu}_I\langle\Phi|\frac{S(r)}{r^3}\left[\vec{s} - 3(\vec{s}\,\hat{\vec{r}})\,\hat{\vec{r}}\right]|\Phi\rangle. \tag{12}$$

The contact interaction is ($\mathcal{B}$ 32)

$$E_c = -\frac{8\pi}{3}\mu_B\,\vec{\mu}_I\,\vec{m}_{av};\ \vec{m}_{av} = \int dr'\delta_T(r')\vec{m}(r'), \tag{13}$$

where

$$\vec{m}(r') = \langle\Phi|\vec{\sigma}\,\delta(\vec{r} - \vec{r}')|\Phi\rangle \tag{14}$$

$\sigma$ are the Pauli matrices,

$$\delta_T(r) = \frac{1}{4\pi r^2}\frac{r_T/2}{[(1 + \epsilon/2mc^2)r + r_T/2]} \tag{15}$$

$r_T = Ze^2/mc^2$ is the Thomas radius.

By comparison with (4) we get the expressions for the hyperfine fields $\vec{B}_{orb}$, $\vec{B}_{dip}$ and $\vec{B}_c$:

$$\vec{B}_{orb} = 2\mu_B\langle\Phi|\frac{S(r)}{r^3}\vec{l}\,|\Phi\rangle \tag{16}$$

$$\vec{B}_{dip} = 2\mu_B\langle\Phi|\frac{S(r)}{r^3}\left[3(\vec{s}\,\hat{\vec{r}})\,\hat{\vec{r}} - \vec{s}\right]|\Phi\rangle, \tag{17}$$

$$\vec{B}_c = \frac{8\pi}{3}\mu_B\,\vec{m}_{av} \tag{18}$$

In Blügel *et al.* formulation contact field is parallel to the spin density on nucleus. Note that assuming that $\vec{m}_{av} = 2\vec{s}$ $B_c$ of $\mathcal{A}$ equals to $-B_c$ of $\mathcal{B}$.

In nonrelativistic limit $S(r) = 1$ and comparison with eqs. (5, 6) shows that in all cases the Abragam and Bleaney hyperfine fields are negative of Blügel *et al.* hyperfine fields.

Assuming that $\vec{B}_{dip}$ arises from electrons with orbital moment $l$, (17) may be recast by using the equivalent operators ($\mathcal{A}$, 17.43, 17.44 I did not check it and the sign in following eq. seems to me suspicious, but I do not believe that $\mathcal{A}$ will carry such mistake to all the following formulae.)

$$3(\vec{s}\vec{\hat{r}})\vec{\hat{r}} - \vec{s}\,, \longrightarrow \frac{2}{(2l+3)(2l-1)}\left[l(l+1)\vec{s} - \frac{3}{2}(\vec{l}\,\vec{s})\,\vec{l} - \frac{3}{2}\vec{l}\,(\vec{l}\,\vec{s})\right] \tag{19}$$

which gives

$$\vec{B}_{dip} = \frac{4\mu_B}{(2l+3)(2l-1)}\langle\Phi|\frac{S(r)}{r^3}\left[l(l+1)\vec{s} - \frac{3}{2}(\vec{l}\,\vec{s})\,\vec{l} - \frac{3}{2}\vec{l}\,(\vec{l}\,\vec{s})\right]|\Phi\rangle \tag{20}$$

**Conclusion: comparison of $\mathcal{A}$ and $\mathcal{B}$ shows that the sign of the hyperfine field as given by $\mathcal{A}$ is opposite to the one given by $\mathcal{B}$.**

The projections of $\vec{B}_{orb}$, $\vec{B}_{dip}$ on the quantization axis $\zeta$ are

$$B_\zeta^{orb} = 2\mu_B\langle\Phi|\frac{S(r)}{r^3}l_\zeta\,|\Phi\rangle, \tag{21}$$

$$B_\zeta^{dip} = \frac{4\mu_B}{(2l+3)(2l-1)}\langle\Phi|\frac{S(r)}{r^3}\left[l(l+1)s_\zeta - \frac{3}{2}(\vec{l}\,\vec{s})\,l_\zeta - \frac{3}{2}l_\zeta\,(\vec{s}\,\vec{l})\right]|\Phi\rangle \tag{22}$$

### C. $B_c$ in WIEN code

$B_c$ is calculated by program MIXER. First, the subroutine HYPER calculates the electron density $hyperf$ at the spherical slab around the nucleus

$$hyperf = \frac{q_{el}}{\frac{4}{3}\pi(r_T^3 - r_1^3)}\,, \tag{23}$$

where $q_{el}$ is number of electrons in the spherical slab

$$q_{el} = \int_{r_1}^{r_T} \rho_{00}(r)dr \tag{24}$$

$\rho_{00}$ is the spherical component of the radial density, $r_T$ is Thomas radius, $r_1$ is the first point in spherical mesh of given atom. $hyperf$ has three indexes: $hyperf(atom, elc, spin)$, $elc$= 1,2,3,4 correspond to valence, semicore, core and total density, $spin$=1,2 corresponds to ↑, ↓. Afterwards in the main program MIXER $B_c$ is calculated in kG:

$$B_c(atom, elc) = 524.3\,[hyperf(atom, elc, 1) - hyperf(atom, elc, 2)]\,. \tag{25}$$

**Conclusion: $B_c$ in WIEN has the same sign as the spin density and it corresponds to Blügel *et al.* approach.**

## II. $B_{orb}$ AND $B_{dip}$ IN VERSION 5 OF WIEN2K

### A. Mean value of on-site operators

Equations (16,20) require evaluation of the mean value of a single particle operator $\hat{O}(r, \vec{l}, \vec{s})$ that belongs to a specific atom. We'll neglect any contributions beyond corresponding atomic sphere. Total mean value is then the sum over orbital numbers (note that we neglect the contribution nondiagonal in $l$, i.e. the crossterms $\langle l, m|\hat{O}|l'm'\rangle$; $l \neq l'$). The population matrix that is calculated by the program LAPWDM may then be used to evaluate the mean value.

### B. Population matrix

In the atomic spheres the basis functions are atomic-like. As a consequence their angular part is described by spherical functions $Y_{lm}(\hat{r})$. The Kohn-Sham eigenfunctions $\varphi_i$ are linear combinations of the basis functions, thus in a given atomic sphere they may be represented as linear combinations of $Y_{lm}(\hat{r})$ too. The population matrix $\hat{n}_l$ is defined as an operator in the $|l, m, \sigma >$ subspace ($m_l = -l, ...l;\ \sigma = \pm 1/2$) of the atomic-like states. The matrix elements of $\hat{n}_l$ are (we adopt here the definition used by Shick *et al.* [4] eq. 12)

$$\hat{n}_{l,m\sigma,m'\sigma'} = \sum_{\varepsilon_i \le E_F} \langle l, m, \sigma|\varphi_i\rangle\langle\varphi_i|l, m', \sigma'\rangle \tag{26}$$

The population matrix is hermitean: $n_{l,m\sigma,m'\sigma'} = (n_{l,m'\sigma',m\sigma})^*$. The cross terms $\sigma = \mp 1/2$, $\sigma' = \pm 1/2$ are nonzero when the spin-orbit interaction is present or the system has noncollinear spins. In WIEN the population matrix is calculated in the local coordinate system of given site.

### C. Mean value

The mean value of the single particle operator $\hat{O}$ may be expressed as

$$\langle\Phi|\hat{O}|\Phi\rangle = \sum_{\varepsilon_i \le E_F} \langle\varphi_i|\hat{O}|\varphi_i\rangle. \tag{27}$$

Assuming that $\hat{O}$ is nonzero within the atomic sphere only and neglecting the terms nondiagonal in $l$, this may be rewriten as

$$\begin{aligned} &\sum_{\varepsilon_i \le E_F} \sum_{lmm'}^{\sigma\sigma'} \langle\varphi_i|lm\sigma\rangle\langle lm\sigma|\hat{O}|lm'\sigma'\rangle\langle lm'\sigma'|\varphi_i\rangle = \\ &\sum_{lmm'}^{\sigma\sigma'} \hat{O}_{lm\sigma,lm'\sigma'} \sum_{\varepsilon_i \le E_F} \langle\varphi_i|lm\sigma\rangle\langle lm'\sigma'|\varphi_i\rangle = \\ &\sum_{lmm'}^{\sigma\sigma'} \hat{O}_{lm\sigma,lm'\sigma'}\hat{n}_{l,m'\sigma',m\sigma} = \sum_l \mathrm{Tr}\,(\hat{n}_l\hat{O}). \end{aligned} \tag{28}$$

## III. IMPLEMENTATION TO WIEN2K

### A. Population matrix

Population matrices $\hat{n}_l$ are calculated by the package LAPWDM. The input data are described in Table I.

The principal subroutine is L2MAIN that is shortened and modified version of L2MAIN of the LAPW2 package. L2MAIN calls subroutine XSPLT that calculates the unsymmetrized matrix

$$xqtl(ly, lpy, mu, ii, nd) = \sum_{\varepsilon_i \le E_F} \langle\varphi_i|lm'\sigma'\rangle\langle lm\sigma|\varphi_i\rangle \tag{29}$$

where $mu$ is index of equivalent atom, $nd = 1..N_l$ is index, specifying the orbital number. Indices $ly = m+l+1$, $lpy = m'+l+1$ numerates $m$, $m'$, acquiring values $1 \le ly, lpy, \le 2l+1$. $ii$ is the spin index in the calculation with the spin-orbit:

$ii = 1, 2, 3$ corresponds to the sequence $\langle\uparrow|\uparrow\rangle$ ,$\langle\uparrow|\downarrow\rangle$ ,$\langle\downarrow|\downarrow\rangle$. Matrix $\hat{xqtl}$ is hermitean conjugated to matrix $\hat{n}$ defined by (26).

Note that because complete calculation of $xqtl$ is done within the loop over the atom types, $xqtl$ has no index specifying the type of the atom.

Matrix $xqtl$ is then symmetrized by applying to it all symmetry operations as listed in struct file, summing the results and dividing it by the number of symmetry operations. The details of symmetrization depend on whether calculation is with or without the s-o coupling and whether it is spin-polarized or not.

| | |
|---|---|
| $E_{min}$ | only eigenfunctions with $\varepsilon_i \geq E_{min}$ will be considered |
| $N_{atoms}$ | number of atom types for which $\hat{n}$ will be calculated |
| $iatom,\ N_l,\ (l_1..l_{N_l})$ | index of atom type, number of $l'$s, orb. numbers. |
| $k_{rad},\, k_{ls}$ | $r$-index and $(l,s)$-index identifying operator $\hat{O}$. |

TABLE I: Input data for LAPWDM. Last line is added *only* if calculation of $\hat{O}$ mean value is required. Third line is repeated $N_{atom}$ times, $E_{min}$ is important in case when it is desirable to obtain $\hat{n}$ separately for valence and semicore states (represented by local orbitals).

| $krad$ | $\hat{O}_r$ | $kls$ | $\hat{O}_{ls}$ |
|---|---|---|---|
| 1 | $\hat{I}$ | 1 | $\hat{I}$ |
| 2 | $r^{-3/2}\,\hat{P}$ | 2 | $\hat{s}_\zeta$ |
| 3 | $r^{-3/2}\,\hat{P}$ | 3 | $\hat{l}_\zeta$ |
| | | 4 | $3\,\hat{l}_\zeta^2 - l\,(l+1)$ |
| | | 5 | $\frac{2}{(2l-1)(2l+3)}\left[3\,\hat{l}_\zeta^2 - l\,(l+1)\right]s_\zeta$ |

TABLE II: Operators corresponding to $krad$ and $kls$ input. $\hat{P}$ is projector on the large component of the relativistic wave function.

The output of standard LAPWDM calculation are the matrices $x\hat{q}tl = \hat{n}_l^+$, the mean value of spin and orbital operator $\langle\vec{s}\rangle, \langle\vec{l}\rangle$ and their projection on the direction of magnetization (for s-o calculation) as specified in case.inso file.

### B. Mean value of operator $\hat{O}_l$

Within the subspace $|lm\rangle$ with $l$ fixed, we may use the equivalent operator approach (see [2] eq. 17.44) and express:

$$\vec{s} - 3(\vec{s}\,\vec{\hat{r}}\,)\,\vec{\hat{r}} = \frac{2}{(2l+1)(2l-1)}\left[l(l+1)\vec{s} - \frac{3}{2}\vec{l}\,(\vec{l}\,\vec{s}\,) - \frac{3}{2}(\vec{l}\,\vec{s}\,)\vec{l}\,\right]. \tag{30}$$

Operators in (16, 17) are then products of $|\vec{r}|$ and $\vec{l}$, $\vec{s}$ dependent operators:

$$\hat{O} = \hat{O}_r\,\hat{O}_{ls}. \tag{31}$$

For $l$ fixed, the radial parts of the basis functions $u_l(r)$, $\dot{u}_l(r)$, ev. local orbitals are $m$-independent. *Providing the relativistic correction is neglected (i.e.* $S(r) = 1$ *in eqs. 16, 17)*, the radial and angular parts of $\langle\hat{O}\rangle$ may be calculated outside the loop over the eigenvectors. This is performed in subroutines RADINT and COUPLX. The data $krad, kls$ specifying $\hat{O}_r$, $\hat{O}_{ls}$ are given in the last line of the input file. Possible values of $krad, kls$ and corresponding operators are listed in Table II. Any allowed $krad$ could be combined with any allowed $kls$ so that e.g. $krad = 1, kls = 2$ corresponds to $s_\zeta$ operator.

To calculate $B_\zeta^{dip}$ it is assumed that $\vec{l} \parallel \vec{s} \parallel \zeta$. (32) then reduces to:

$$B_\zeta^{dip} = \frac{4\mu_B}{(2l+3)(2l-1)}\langle\Phi|\frac{S(r)}{r^3}\,s_\zeta\left[l(l+1) - 3\,l_\zeta^2\right]|\Phi\rangle \tag{32}$$

To obtain $B_{orb}$ in T from the mean value of operator in Tab. 2, specified by $krad = 3$, $kls = 3$ this mean value should be multiplied by factor 12.5169.

*To obtain* $B_{dip}$ *in T from the mean value of operator in Tab. 2, specified by* $krad = 3$, $kls = 5$ *this mean value should be multiplied by factor* **-12.5169.**

### C. Approximations

Below the approximation made are summarized

- Relativistic mass enhancement is neglected ($S(r) = 1$ assumed). This is good approximation for $3d$ atoms, worse for RE and bad for actinides [3]. It could be corrected, but some programming is necessary. Note that relativistic mass enhancement was included in the AVERX program of WIEN97.
- When calculating $B_{dip}$

$$\vec{l}\,\vec{s} = l_\zeta s_\zeta \tag{33}$$

  was assumed. This may be corrected easily and I'll do it.
- Further assumption was that

$$\langle \hat{O}(r)\hat{O}(\vec{l},\vec{s})\rangle = \langle \hat{O}(r)\rangle\langle \hat{O}(\vec{l},\vec{s})\rangle. \tag{34}$$

  I do not know how difficult it would be to correct this approximation.
- Contributions from the interstitial and from $\langle l||l'\rangle$ terms were neglected.

## IV. APPENDIX: CALCULATION OF $Tr(\hat{O}\hat{n}_l)$

Calculation of $Tr(\hat{O}\hat{n}_l)$ is performed in output.f of LAPWDM package. Relevant part is given below. Two points to note:
calculation holds only for $\hat{O}$ for which the crossterms $\langle\uparrow|\hat{O}|\downarrow\rangle = 0$.
$\hat{O}$ has inverted sequence of spin indexes relative to $\hat{n}_l$:
$O_{11} = \langle\downarrow|\hat{O}|\downarrow\rangle$, $O_{12} = \langle\downarrow|\hat{O}|\uparrow\rangle$, $O_{22} = \langle\uparrow|\hat{O}|\uparrow\rangle$.

```
! for <|X|> calculation replace usym by usym*coup
      N=2*LL+1
      if(krad.ne.0)then
! coup has inverted order 1 ... dn, 2 ... up and is diagonal in spin
       do ii=1,3
        do i=1,n
         do j=1,n
          mj=j-ll-1
          uhelp(i,j,ii)=czero
           do k=1,n
            mk=k-ll-1
            if(ii.eq.1)then
            uhelp(i,j,ii)=uhelp(i,j,ii)+usym(i,k,ii)*coup(ll,mj,mk,2,2)
            else if(ii.eq.3)then
            uhelp(i,j,ii)=uhelp(i,j,ii)+usym(i,k,ii)*coup(ll,mj,mk,1,1)
            endif
           enddo
         enddo
        enddo
       enddo
```

*usym* is symmetrized *xqtl* and therefore
$uhelp = \hat{O}\hat{xqtl}^{+} = \hat{O}\hat{n}$

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