

Relativistic calculation of the orbital hyperfine splitting in complex microscopic structures

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Abstract. Theoretical spectroscopy based on double perturbation theory is typically challenged by systems with large orbital hyperfine splitting. Therefore, we here derive a rigorous, non-perturbative scheme starting from Dirac's equation which allows to calculate the contribution of the orbital HFI for complex structures including heavy atoms with strong spin-orbit coupling (SOC). Using the PAW formalism, the method has been implemented in the software package QUANTUM ESPRESSO. We show that the 'orbital part' actually scales with SOC strength if orbital quenching is hindered by low local symmetry, i.e. in case of dimers or atoms at surfaces. This holds true in particular when the unpaired electron is localized in quasi-atomic *p*-like orbitals. Here, the orbital part is by far not negligible, but becomes dominant by surpassing the dipolar contribution by a factor of five.

1. Introduction

The hyperfine splitting of a given system is caused by the interaction of the electronic spin with the magnetic moments of the nuclei and leads to comparably small energy shifts (in the MHz range) in the absorption spectra. It is directly accessible in magnetic resonance (EPR) experiments and has been predicted theoretically via density functional theory (DFT) for decades. In many cases, e.g. for the famous nitrogen-vacancy center, NV⁻ in diamond [1] and in silicon carbide [2], a direct comparison of experimental and theoretical data allows for structure identification. In general, the energy shifts of the hyperfine structure can be separated into three contributions [3]: the isotropic Fermi contact, the anisotropic dipolar and the orbital part. In many systems, especially in semiconductors, the hybridization and deformation of the atomic orbitals by the crystal field leads to the orbital moment being no longer well defined, but effectively averaged out. This so-called orbital quenching occurs in many, but not all relevant physical systems. In this work a



non-perturbative method to calculate the orbital hyperfine splitting is developed which is implemented in the software package QUANTUM ESPRESSO (QE). By simulating different structures, we show that recent reports of DFT failing in hyperfine prediction can actually be attributed to the fact that the orbital term has been neglected in cases with suppressed orbital quenching. Furthermore we analytically derive ratio rules for the orbital and dipolar part of the hyperfine splitting of quasi-atomic single-electron states.

The paper is organized as follows. In Section 2 the non-perturbative 'orbital magnetization' scheme for the calculation of the orbital contribution to the hyperfine splittings is derived, and its implementation (full scheme and the so-called 'reconstruction-only' version) in the QUANTUM ESPRESSO package [4, 5] is described. In section 3.2 the new scheme is evaluated against finite systems, the molecular data is obtained with the ORCA [6, 7] quantum chemistry code. Further evaluation becomes possible via one-electron atomic systems, for which relativistic angular-momentum (j-) depending ratio rules are analytically derived (Section 3.1). Finally, the non-perturbative approach is applied to 3D and 2D periodic crystalline systems, i.e. ferromagnetic iron (Section 4.1) and isolated Pb atoms adsorbed at MgO/Ag(111) substrates (Section 4.2), showing that the 5:1 ratio rule for $p_{3/2}$ electrons is also valid in the latter case.

2. Theoretical Background

In this section, a derivation of the hyperfine splitting operators based on the calculation of the hyperfine splitting energies by Blügel et al. [3] is given and the theory of the hyperfine tensor $\underline{A}$ is presented. Additionally, the orbital hyperfine splitting within the framework of double perturbation theory is briefly discussed and a novel approach to calculate the orbital part of the hyperfine tensor (orbital magnetization scheme) is presented.

The nucleus' magnetic moment $\vec{\mu}_I$ leads to a vector potential

$$\begin{aligned}\vec{A}(\vec{r}) &= \frac{\mu_0}{4\pi} \nabla \times \frac{\vec{\mu}_I}{r} \\ &= \frac{\mu_0}{4\pi} \vec{\mu}_I \times \frac{\vec{r}}{r^3}.\end{aligned}$$

Instead of solving the exact Dirac's Equation for one electron in an external potential V , given by [8]

$$\left[c\vec{\alpha} \cdot \vec{p} - ec\vec{\alpha} \cdot \vec{A}(\vec{r}) + \beta mc^2 + V \right] \Psi^{\text{rel}} = E\Psi^{\text{rel}},$$

one can use first-order relativistic perturbation theory in order to estimate the energy shift due to the hyperfine splitting

$$\Delta E_{\text{hyperfine}} = -ec\langle \Psi^{\text{rel}} | \vec{\alpha} \cdot \vec{A}(\vec{r}) | \Psi^{\text{rel}} \rangle. \quad (1)$$

Blügel et al. have shown, based on the work of Breit [9], that the hyperfine correction according to Equation 1 for a radial symmetric potential V consists of three terms [3]

$$\Delta E_{\text{hyperfine}} = \Delta E_{\text{orbital}} + \Delta E_{\text{dipolar}} + \Delta E_{\text{contact}}$$

with

$$\begin{aligned}
\Delta E_{\text{orbital}} &= -\frac{e}{m} \frac{\mu_0}{4\pi} \vec{\mu}_I \cdot \langle \Psi_L | \frac{S(r)}{r^3} \hat{L} | \Psi_L \rangle \\
\Delta E_{\text{dipolar}} &= \frac{e\hbar}{2m} \frac{\mu_0}{4\pi} \langle \Psi_L | \frac{S(r)}{r^3} [\hat{\sigma} \cdot \vec{\mu}_I - 3(\hat{\sigma} \cdot \vec{e}_r)(\vec{\mu}_I \cdot \vec{e}_r)] | \Psi_L \rangle \\
\Delta E_{\text{contact}} &= -\frac{8\pi}{3} \frac{e\hbar}{2m} \frac{\mu_0}{4\pi} \langle \Psi_L | S(r) \hat{\sigma} \vec{\mu}_I \cdot \delta(\vec{r}) | \Psi_L \rangle \\
&\quad - \frac{e\hbar}{2m} \frac{\mu_0}{4\pi} \langle \Psi_L | \frac{1}{r^2} \frac{\partial S}{\partial r} [\hat{\sigma} \cdot \vec{\mu}_I - (\hat{\sigma} \cdot \vec{e}_r)(\vec{\mu}_I \cdot \vec{e}_r)] | \Psi_L \rangle
\end{aligned} \tag{2}$$

Here, $\hat{L}$ denotes the angular momentum operator, $\vec{\sigma}$ contains the Pauli matrices $\vec{\sigma} = \begin{bmatrix} \sigma_x \\ \sigma_y \\ \sigma_z \end{bmatrix}$ and $S(r)$ is the so-called relativistic form function given by $S(r) = \frac{2mc^2}{2mc^2 + E - V(r)}$, which describes the reciprocal of the relativistic mass enhancement.

$\Delta E_{\text{contact}}$ gives rise to a purely isotropic term (the so-called Fermi contact term), whereas $\Delta E_{\text{dipolar}}$ determines the anisotropic part. The orbital term ($\Delta E_{\text{orbital}}$) can contribute to both isotropic and anisotropic parts, but is usually left out by referring to orbital quenching due to the crystal field of the surrounding host lattice. In principle, only the large component is required to evaluate the expectation values in Equation 2. By substituting $S(r) \rightarrow 1$ and using a renormalized scalar wave function Ψ instead of the large component Ψ_L of the relativistic four-component spinor $\Psi^{\text{rel}} = \begin{bmatrix} \psi_L \\ \psi_S \end{bmatrix}$, one obtains the following scalar formula for the orbital hyperfine energy shift

$$\Delta E_{\text{orbital}} = -\frac{e}{m} \frac{\mu_0}{4\pi} \vec{\mu}_I \cdot \langle \Psi | \frac{1}{r^3} \hat{L} | \Psi \rangle = \langle \hat{H}_{\text{orb}} \rangle, \tag{3}$$

whereby the orbital hyperfine operator may be written as

$$\hat{H}_{\text{orb}} = -\frac{e}{m} \frac{\mu_0}{4\pi} \vec{\mu}_I \frac{1}{r^3} \hat{L}. \tag{4}$$

In the following, the orbital hyperfine splitting operator in Equation 4 is considered. Instead of directly calculating the corresponding energy shift due to the magnetic field of the nucleus as in Equations 2 and 3, the hyperfine splitting of a system can be described with the help of its hyperfine tensor $\underline{A}$

$$A_{lm} = \frac{\partial^2 \Delta E_{\text{hyperfine}}}{\partial S_l \partial I_m} = \frac{\partial^2 \langle \hat{H}_{\text{hyperfine}} \rangle}{\partial S_l \partial I_m}. \tag{5}$$

Usually, the contributions to this hyperfine tensor are calculated with double perturbation theory (DPT). The corresponding orbital part is then given by

$$A_{lm}^{\text{orbital}} = \text{Re} \sum_{i,j \neq i} \frac{\langle \hat{H}_{\text{SOC}}^l \rangle_{ij} \langle \hat{H}_{\text{orb}}^m \rangle_{ji}}{E_j^{0,0} - E_i^{0,0}} = \frac{\mu_0}{4\pi} \frac{e\hbar}{4m^3c^2} \mu_N g_N \frac{1}{S} \text{Re} \left(\sum_{i,j \neq i} \frac{\langle \Psi_i^{0,0} | \frac{1}{r} \frac{\partial V}{\partial r}(r) \hat{L}_l \hat{S}_z | \Psi_j^{0,0} \rangle \langle \Psi_j^{0,0} | \frac{1}{r^3} \hat{L}_m | \Psi_i^{0,0} \rangle}{E_j^{0,0} - E_i^{0,0}} \right) \quad (6)$$

and arises from nucleus-orbit ($\hat{H}_{\text{orb}}$) as well as spin-orbit coupling ($\hat{H}_{\text{SOC}}$) [10]. The expectation value for A_{lm} in Equation 6 is calculated with respect to the system's unperturbed wave functions $|\Psi_i^{0,0}\rangle$, which are solutions of a Hamiltonian *without* SOC. The latter is viewed as one of the perturbing operators within the formalism of double perturbation theory. DPT is especially problematic if metallic systems are considered, because of the energy denominator in Equation 6 approaching or being zero.

2.1. "Orbital magnetization scheme"

Now, the focus is turned toward a new non-perturbative implementation of the orbital part of the hyperfine splitting in the software package QUANTUM ESPRESSO (QE) [4, 5].

The orbital part of the hyperfine tensor $A_{lm}^{\text{orbital},a}$ of nucleus a is implemented in a manner analogous to the orbital magnetization and to the Δg -tensor (see Ref. [11]). In the following, this implementation shall hence be referred to as orbital magnetization scheme.

$A_{lm}^{\text{orbital},a}$ can be written as

$$A_{lm}^{\text{orbital},a} = \frac{\partial^2 E_{\text{hyperfine, orbital}}^a}{\partial S_l \partial I_m^a} \quad \text{with } E_{\text{hyperfine, orbital}}^a = -\frac{e}{m} \frac{\mu_0}{4\pi} \mu_N g_N^a \left\langle \frac{\hat{\vec{L}} \cdot \hat{\vec{I}}}{r_a^3} \right\rangle.$$

Three independent Kohn-Sham equations with the scalar relativistic Hamiltonian $\hat{H}_0$ and consideration of SOC in the l^{th} direction (i.e. for $l = 1, 2, 3$) have to be solved

$$(\hat{H}_0 + \Delta \hat{H}_{\text{SOC}}^l) |\Psi_j^l\rangle = \epsilon_j^l |\Psi_j^l\rangle. \quad (7)$$

By this we introduce well-defined quantization axes in cartesian directions like in case of a magnetic field applied in the respective direction. This might alter or influence a system with non-colinear spin, but nicely reflects the situation in magnetic resonance experiments, where the spin of the electronic system is exposed to an external magnetic field. The required SOC is included via

$$\Delta \hat{H}_{\text{SOC}}^l = \frac{e}{2m^2c^2} \hat{\sigma}_l \cdot [\tilde{\nabla} V(\vec{r}) \times \hat{p}]$$

with Pauli spin matrices $\hat{\sigma}_l = \hat{\sigma}_z \vec{e}_l = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \vec{e}_l$ and *reduced* gradient of the potential

$$\tilde{\nabla} V(\vec{r}) := \nabla \left(\frac{2mc^2}{1 - \frac{V(\vec{r})}{2mc^2}} \right) = \frac{1}{\left(1 - \frac{V(\vec{r})}{2mc^2}\right)^2} \nabla V(\vec{r}) \leq \nabla V(\vec{r}) \quad (8)$$

defining the SOC Hamiltonian in the so-called zeroth order relativistic approximation (ZORA), which for heavy atoms essentially corrects the electronic structure to the full relativistic results [12]. Going back to the standard gradient, we obtain the SOC Hamiltonian in Breit-Pauli form, which will be referred to as Pauli SOC in the following. In both cases, the orbital part of the hyperfine tensor can be rewritten as

$$\begin{aligned} A_{lm}^{\text{orbital},a} &= \frac{\partial^2 E_{\text{hyperfine, orbital}}^a}{\partial S_l \partial I_m^a} \\ &= -\frac{e}{m} \frac{\mu_0}{4\pi} \mu_N g_N^a \frac{\partial^2 \langle \frac{\hat{L} \hat{I}^a}{r_a^3} \rangle}{\partial S_l \partial I_m^a} \\ &= \frac{\mathcal{L}_m^a(\vec{e}_l) - \mathcal{L}_m^a(-\vec{e}_l)}{S - (-S)} \\ &= \frac{\mathcal{L}_m^a(\vec{e}_l)}{S}, \end{aligned} \quad (9)$$

where S denotes the total spin of the system and $\mathcal{L}_m^a(\vec{e}_l) := -\langle \frac{e}{m} \frac{\mu_0}{4\pi} \mu_N g_N^a \frac{1}{r_a^3} \hat{L}_m \rangle = \langle \hat{H}_{\text{orb}}^m \rangle$. In the last step the identity $\mathcal{L}_m^a(-\vec{e}_l) = -\mathcal{L}_m^a(\vec{e}_l)$ was used. The remaining expectation value is calculated with respect to the wave functions $|\Psi_n^l\rangle$.

This approach can be directly applied to multi-component relativistic schemes. Also scalar wave functions can be used, but the inclusion of spin-orbit coupling is mandatory, otherwise the expectation value of $\hat{H}_{\text{orb}}$ remains zero.

Equation 9 might be directly evaluated by an all-electron approach. However, we intend in establishing a method that allows to compute the orbital hyperfine splitting for large extended and potentially periodic systems, which leads to using the Projector augmented wave (PAW) formalism. This method introduces smooth pseudo wave functions $\tilde{\Psi}$ that differ inside an augmentation sphere $\Omega_{\vec{R}_a}$ around each atom from the 'true' all-electron wave functions Ψ_{AE} . The latter can be reconstructed from the pseudo wave function via the PAW transformation $\hat{\mathcal{T}}$,

$$\tilde{\Psi} = \hat{\mathcal{T}} \Psi_{\text{AE}} \quad \text{with} \quad \hat{\mathcal{T}} = \hat{1} + \sum_{a,i} (|\Phi_i^a\rangle - |\tilde{\Phi}_i^a\rangle) \langle p_i^a| \quad (10)$$

built-up by system-independent, precalculated basis sets $\{|\Phi_i^a\rangle\}$, $\{|\tilde{\Phi}_i^a\rangle\}$ and projector functions $\{|p_i^a\rangle\}$, non-zero exclusively in the PAW augmentation sphere around the given

nucleus a .

In case of a local operator $\hat{O}$ the expectation value $\langle \hat{O} \rangle$ can then be calculated as

$$\langle \hat{O} \rangle = \sum_n^{\text{occ.}} f_n \langle \tilde{\Psi}_n | \hat{O} | \tilde{\Psi}_n \rangle + \sum_a \sum_{i,j} \sum_n^{\text{occ.}} f_n \langle \tilde{\Psi}_n | p_i^a \rangle o_{a,ij} \langle p_j^a | \tilde{\Psi}_n \rangle, \quad (11)$$

where f_n denotes the occupation numbers, and the matrix elements $o_{a,ij}$ are given by

$$o_{a,ij} = \langle \Phi_i^a | \hat{O} | \Phi_j^a \rangle - \langle \tilde{\Phi}_i^a | \hat{O} | \tilde{\Phi}_j^a \rangle.$$

Equation 11 allows to calculate the all-electron expectation values without the need to calculate the all-electron wave functions, which saves computational time and memory.

If the major part of the expectation value arises from the integration inside the augmentation spheres $\Omega_{\vec{R}^a}$, then the first term and the second part of the second term in Equation 11 are very small and almost cancel each other. This has already been shown for the Fermi-contact operator and spin-orbit coupling [12]

$$\langle \hat{O} \rangle = \sum_{\tilde{a}} \sum_{i,j} \sum_n^{\text{occ.}} f_n \langle \tilde{\Psi}_n^l | p_i^a \rangle \langle \Phi_i^a | \hat{O} | \Phi_j^a \rangle \langle p_j^a | \tilde{\Psi}_n^l \rangle. \quad (12)$$

In case of the local operator $\hat{\mathcal{L}}_m^a$, we arrive at the following formula for the reconstruction only form of the orbital hyperfine splitting

$$A_{lm}^{\text{orbital},a} = -\frac{e}{m} \frac{\mu_0}{4\pi} \mu_N g_N^a \frac{1}{S} \sum_{\tilde{a}} \sum_{i,j} \sum_n^{\text{occ.}} f_n \langle \tilde{\Psi}_n^l | p_i^a \rangle \langle \Phi_i^a | \frac{1}{r_a^3} \hat{L}_m | \Phi_j^a \rangle \langle p_j^a | \tilde{\Psi}_n^l \rangle. \quad (13)$$

As the matrix elements $\langle \Phi_i^a | \frac{1}{r_a^3} \hat{L}_m | \Phi_j^a \rangle$ only have to be calculated once before the self-consistent calculation and no Fourier transformations are required, the calculation of the expectation value according to Equation 13 is extremely efficient and – as will be shown in the following – still accurate and almost equivalent with the full scheme which reads in explicit form

$$A_{lm}^{\text{orbital},a} = -\frac{e}{m} \frac{\mu_0}{4\pi} \mu_N g_N^a \frac{1}{S} \left(\sum_n^{\text{occ.}} f_n \langle \tilde{\Psi}_n | \frac{1}{r_a^3} \hat{L}_m | \tilde{\Psi}_n \rangle + \sum_a \sum_{i,j} \sum_n^{\text{occ.}} f_n \langle \tilde{\Psi}_n | p_i^a \rangle \ell_{a,ij} \langle p_j^a | \tilde{\Psi}_n \rangle \right),$$

where the matrix elements $\ell_{a,ij}$ are given by

$$\ell_{a,ij} = \langle \Phi_i^a | \frac{1}{r_a^3} \hat{L}_m | \Phi_j^a \rangle - \langle \tilde{\Phi}_i^a | \frac{1}{r_a^3} \hat{L}_m | \tilde{\Phi}_j^a \rangle.$$

3. Evaluation of the method - isolated atoms and diatomic molecules

In order to evaluate the new scheme, the hyperfine parameters of several different atoms and diatomic molecules were analyzed. We start with isolated atoms, where the spherically symmetric potential of the nucleus allows for an exact analytic derivation of relativistic ratio rules relating the usually neglected orbital contribution $\Delta E_{\text{orbital}}$ to the standard dipole contribution $\Delta E_{\text{dipolar}}$.

3.1. Relativistic ratio rules

Thanks to the radial symmetric potential $V(r)$ and by using the product ansatz

$$\Psi^{\text{rel}}(\vec{r}) = \begin{bmatrix} \psi_L \\ \psi_S \end{bmatrix} = \begin{bmatrix} g(r)\Omega_{1,j,l,m_j} \\ if(r)\Omega_{2,j,l,m_j} \end{bmatrix} \quad (14)$$

Dirac's equation can be transformed into two differential equations for the radial wave functions $g(r)$ and $f(r)$. Here $\Omega_{1/2,j,l,m_j}$ denote the relativistic spherical harmonics

$$\Omega_{1,j,l,m_j} = \begin{bmatrix} N_1 Y_{l,m_j-\frac{1}{2}}(\vartheta, \varphi) \\ N_2 Y_{l,m_j+\frac{1}{2}}(\vartheta, \varphi) \end{bmatrix} \quad \text{and} \quad \Omega_{2,j,l,m_j} = \begin{bmatrix} N_3 Y_{l,m_j-\frac{1}{2}}(\vartheta, \varphi) \\ N_4 Y_{l,m_j+\frac{1}{2}}(\vartheta, \varphi) \end{bmatrix}.$$

Thus, both components of Ψ^{rel} consist of two-dimensional, relativistic spherical harmonics and radial wave functions [13]. The same ansatz can be used to evaluate the contributions to the hyperfine splittings $\Delta E_{\text{hyperfine}}$ according to Eq. 2 (see Appendix A). Notably, the orbital and dipolar terms turn out to be very similar:

$$\Delta E_{\text{orbital}} = -\frac{e\hbar}{m} \frac{\mu_0}{4\pi} \mu_{I,z} \beta_{\text{orbital}} \int_0^\infty \frac{S(r)}{r} |g(r)|^2 dr,$$

$$\Delta E_{\text{dipolar}} = \frac{1}{2} \frac{e\hbar}{m} \frac{\mu_0}{4\pi} \mu_{I,z} \beta_{\text{dipolar}} \int_0^\infty \frac{S(r)}{r} |g(r)|^2 dr,$$

i.e., they essentially differ only in the angular integrals β_{orbital} and β_{dipolar} . Their ratio thus does not depend on the principal quantum number n . For an isolated (single unpaired) electron, the latter can be analytically evaluated depending on the relativistic quantum numbers j , finally yielding

$$\eta = \frac{\Delta E_{\text{orbital}}}{\Delta E_{\text{dipolar}}} = -2 \frac{\beta_{\text{orbital}}}{\beta_{\text{dipolar}}} = \begin{cases} 2j & \text{for } j = l - 1/2 \\ -2(j+1) & \text{for } j = l + 1/2 \end{cases} \quad (15)$$

Further details of the derivation can be found in Appendix A.

Interestingly, due to the half-integer nature of the total angular momentum quantum number j , the ratios η are always integer (see also Table A2). For single-electron systems the orbital part thus becomes dominant surpassing the standard dipolar contribution by a factor of up to 5, 7 and 9 for p , d , and f electrons, respectively.

Actually, our implementation in QE obeys this 5:1 rule for atomic p -states. The simulation of ionized C, Si, Ge, Sn, and Pb atom (C^+ to Pb^+) with a single unpaired electron in $np_{\frac{3}{2}}$ orbitals result in huge orbital contributions in or close to the GHz range already for carbon. The ratio rule $f_{\text{orbital}}(p_{\frac{3}{2}}) = 5 \cdot f_{\text{dipolar}}(p_{\frac{3}{2}})$ is fulfilled within a few percent (see Table 1), whereby the agreement becomes even better for heavier atoms. In other words, the orbital ratio rules derived for the relativistic hydrogen-like atoms also hold true for p -like spin-distributions of heavier atoms.

Table 1. A^{orbital} and A^{dipolar} along the p -orbital for Pb^+ type atoms (calculated for the reconstruction-only and the full scheme, both while using ZORA and (Breit-)Pauli SOC Hamiltonian).

atom	ZORA			Pauli		
	$A_{\parallel}^{\text{orb}}$ [MHz]		$5 \cdot A_{\parallel}^{\text{dip}}$ [MHz]	$A_{\parallel}^{\text{orb}}$ [MHz]		$5 \cdot A_{\parallel}^{\text{dip}}$ [MHz]
	rec. only	full		rec. only	full	
C^+	-610.3	-624.5	-656.5	-610.3	-624.5	-656.5
Si^+	655.1	662.7	670.0	655.1	662.7	670.1
Ge^+	292.8	294.6	295.9	293.2	295.0	296.2
Sn^+	4971.8	4986.4	4992.9	5018.2	5023.8	5039.4
Pb^+	-6190.0	-6193.7	-6201.6	-6494.6	-6498.3	-6506.3

As expected, the use of ZORA (instead of the Breit-Pauli SOC Hamiltonian) slightly corrects the calculated orbital hyperfine splitting to smaller values, whereby this correction is restricted to quite heavy atoms. Up to Ge^+ , the values calculated by ZORA and Pauli are almost equivalent. Table 1 also shows that the prediction of the reconstruction-only method and the full PAW scheme are basically identical. The resulting numbers depend much more on the choice of some technical details, like the size of the PAW augmentation sphere for the respective pseudopotential as determined by the so-called cut-off radius R_{cut} .

Furthermore, $A_{\text{rec-only}}^{\text{orbital}}$ and $A_{\text{full}}^{\text{orbital}}$ are independent of the used pseudopotential, as can be seen from Figure 1:

As a prototype example, the ionized Pb atom, Pb^+ , with total spin $S = 1/2$ and unpaired electron in a $5p_{\frac{3}{2}}$ orbital shall be considered. Here, the cut-off radius R_{cut} can be varied in a comparatively wide range from 2.6 to 3.9 Bohr radii r_B . As can be seen from Figure 1 the resulting orbital contributions to the hyperfine splittings differ by more than 10%. Independent of the exact choice of R_{cut} , however, the orbital hyperfine splitting as calculated with QE fulfills the analytically obtained rule $f_{\text{orbital}}(p_{\frac{3}{2}}) = 5 \cdot f_{\text{dipolar}}(p_{\frac{3}{2}})$. This demonstrates that the dependence of the hyperfine values from the cut-off radius cannot be fully eliminated by using the full scheme. On the other hand, this result further confirms the conclusion that the reconstruction-only form provides an efficient and still accurate approach to calculate the orbital contribution.

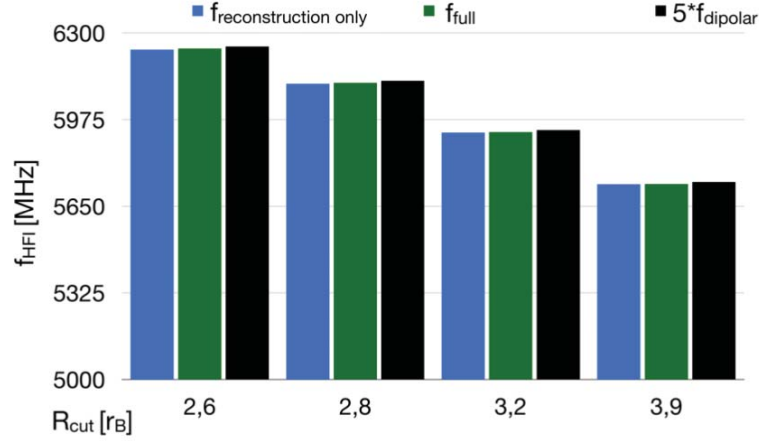


Figure 1. Pb^+ atom: $A_{\parallel}^{\text{orbital}}$ calculated with the full and the reconstruction only form together with $5 \cdot A_{\parallel}^{\text{dipolar}}$ for different cut-off radii is displayed. It is clearly visible that the analytically derived ratio rule $f_{\text{orbital}}(p_{\frac{3}{2}}) = 5 \cdot f_{\text{dipolar}}(p_{\frac{3}{2}})$ holds true.

The importance of the ratio rules should not be underestimated. They cover special, but in particular those situations where orbital quenching is hindered, resulting in non-vanishing orbital contributions to the hyperfine splitting, introducing huge additional anisotropies in the GHz range. Experimentalists might use this results for approximate corrections to empirical estimates for the hyperfine splittings, if the unpaired electron, i.e. the spin distribution is in fact localized in atom-like orbitals.

In the following we want to illustrate this by applying the ratio rules for determining an estimate for an excited hydrogen atom, where the electron is in a $2p_{\frac{1}{2}}$ orbital. Calculation

Table 2. Hyperfine splitting (frequency in MHz) of the excited $2p_{\frac{1}{2}}$ state of hydrogen, determined via various schemes (for further details see text)

$f(2p_{\frac{1}{2}})$		
exact relativistic analytics		59.2 MHz
QE (numerical)	via Eq. 16	63.7 MHz
analytic perturbation theory		59 MHz ¹

of A^{orb} and thus of the full hyperfine tensor provides a challenge for a scalar relativistic approach, but using the 1:1 ratio rule for $p_{\frac{1}{2}}$ electrons, this problem can be circumvented. First, the contribution from $\Delta E_{\text{contact}}$ to the hyperfine splitting for the single electron $2p_{\frac{1}{2}}$ state can be expected to be negligibly small, (numerically it is approximately 10^{-5} times smaller than the orbital and dipolar contribution). Therefore it is justified to calculate the hyperfine splitting frequencies of this state as:

$$\begin{aligned} f(2p_{\frac{1}{2}}) &= f^{\text{orbital}}(2p_{\frac{1}{2}}) + f^{\text{dipolar}}(2p_{\frac{1}{2}}) \\ &= 2f^{\text{dipolar}}(2p_{\frac{1}{2}}). \end{aligned} \quad (16)$$

The hyperfine splitting frequency for the $2p_{\frac{1}{2}}$ excited state of a H atom is numerically calculated according to Equation 16 with the standard approach implemented in QE. In Table 2 the result is compared with the result of two analytical methods, (i) an exact fully relativistic treatment (to be published elsewhere) and (ii) analytic perturbation theory based on Schrödinger's theory, where the spin-orbit coupling constants are fitted to experiment. In all cases, the hyperfine frequency parallel to the z -axis, i.e. $f(2p_{\frac{1}{2}}) = A_{zz}^{\text{orbital}}$, is given. The agreement between both analytic reference values and the one from the approximative formula Eq. 16 is excellent, confirming again the validity of the ratio rules and illustrating their benefit for many potential applications. In section 4.2 we will show that the ratio rules also hold in case of single atoms adsorbed at semiconductor surfaces.

3.2. Comparison of new scheme with ORCA - molecules

Before applying the new method to extended periodic systems, in order to further broaden the basis for an evaluation of the new method, a set of small molecular systems are investigated. The finite size of the test systems allows for direct comparison with an all-electron approach as available by the quantum chemistry ORCA software package [6, 7]. The calculation of the hyperfine splitting in ORCA, in particular the orbital contribution, is based on double perturbation theory (DPT)[14]; the used SOC operator is an effective one-electron operator with effective charges provided by Koseki *et al.* [14], [15], [16], [17]. In contrast to that, our implementation in QE provides a non-perturbative SOC scheme. Further technical details of the molecular calculations may be found in Appendix B.

For this comparative study, we chose a set of representative diatomic molecules, also used in Ref. [18] to evaluate the spin-orbit contribution to the zero-field splitting (ZFS). The molecules cover a wide range of atomic species in different spin states, including high-spin states up to $S = 5/2$. The explicit data for the principle values of the A^{orbital} tensor are given in Table B3 (see Appendix). They are also illustrated in Figure 2, where the $A_{\perp}^{\text{orbital}}$ values calculated within the reconstruction-only and the full scheme are shown to be

basically identical; $A_{\text{rec-only}}^{\text{orbital}} = A_{\text{full}}^{\text{orbital}}$ holds true irrespective of the mass of the molecules. We briefly note that this equality does not change when the Pauli instead of the ZORA formalism is used.

Furthermore, the values calculated with QE and ORCA agree well, including qualitative trends and the signs. The deviation between the absolute values is mostly below 15%. Larger percentual deviations are only observed for small values below 10 MHz, where the deviations between QE and ORCA are below 1.5 MHz. We briefly note that the same agreement is found for other molecular high-spin states (total spin up to $S = 3$, FeI^+ , see also Appendix Table B10), where also data for FeI , FeI_2^+ and Fe_2^+ molecules are listed. The deviations are always quite small and comparable to that obtained for the already established orbital magnetization approach for Δg . Notably the deviations are independent on the spin state, emphasising in particular the accordance with respect to total-spin (S) dependent prefactors.

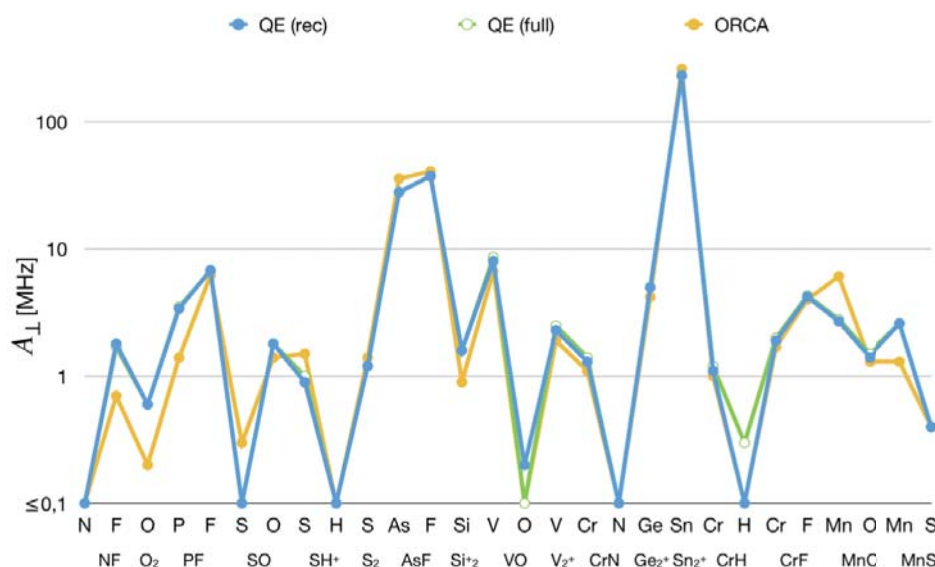


Figure 2. Principal values of the A^{orbital} tensor calculated for a representative set of molecules from Ref. [18] with spin $S = 1$ (NF, O₂, PF, SO, SH, S₂, AsF), spin $S = \frac{3}{2}$ (Si₂⁺, VO, V₂⁺, CrN, Ge₂⁺, Sn₂⁺) and spin $S = \frac{5}{2}$ (CrH, CrF, MnO, MnS). Both versions of the new approach (reconstruction-only, *blue* and the full scheme, *green*) are given and compared with the quantum chemistry code ORCA, *yellow*. Explicit data is provided in Table B4 (see Appendix).

For the molecules of the Pb_2^{3+} family, the calculation of $A_{\perp}^{\text{orbital}}$ with ORCA and QE yields matching results for almost all molecules (see also Figure 3). Only the heaviest dimers (Pb_2^{3+}) show a considerable deviation between $A_{\perp}^{\text{orbital, QE}}$ and $A_{\perp}^{\text{orbital, ORCA}}$ up to a factor of two. This can also be seen from Table 3 which enlists the values of A^{orbital} calculated with ORCA and QE for these dimers. The parallel component of the orbital hyperfine tensor is affected by *orbital quenching*. It equals exactly 0 MHz in case of the QE calculation. The ORCA calculation, however, shows this result only in case of the lighter atoms. The non-vanishing value of $A_{\parallel}^{\text{orbital}}$ for the heavier dimers in ORCA can be attributed to numerical noise. In QE the zero-values are ensured by applying group theory and a related symmetrization of the wave functions.

Table 3. A^{orbital} for dimers of the Pb_2^{3+} -family. With QE the value along the dimer bond is exactly zero, independent on the calculation scheme.

dimer	$A_{\perp}^{\text{orbital}}$ [MHz]					$A_{\parallel}^{\text{orbital}}$ [MHz]	
	ORCA	$A_{\perp}^{\text{orbital, QE (rec.)}}$		$A_{\perp}^{\text{orbital, QE (full)}}$		ORCA	$A_{\parallel}^{\text{orbital, QE (rec/full)}}$
		ZORA	Pauli	ZORA	Pauli		
C_2^{3+}	-0.6	-0.8	-0.8	-0.8	-0.8	0.0	0.0
Si_2^{3+}	2.9	4.0	4.0	4.1	4.1	0.0	0.0
Ge_2^{3+}	10.7	11.2	11.8	11.4	11.9	0.1	0.0
Sn_2^{3+}	600.2	542.1	615.8	546.4	620.8	3.3	0.0
Pb_2^{3+}	-3126.7	-1586.8	-2140.1	-1590.4	-2141.9	-8.1	0.0

Given the very good agreement in almost all cases, the factor-of-2 deviation in case of the Pb_2^{3+} dimer appears astonishing. Hints on the origin might be given by analyzing the influence of details of the SOC treatment. The QE-calculations for the molecules of the Pb_2^{3+} -family are thus repeated by using the Pauli instead of the ZORA formalism in QE (see Figure 3). The resulting values can also be found in Table 3. As expected, they do not change for lighter dimers. In case of Sn_2^{3+} and Pb_2^{3+} , however, $A_{\perp}^{\text{orbital}}$ changes considerably when the employed SOC formalism is altered. As a consequence, the QE-values obtained using the Pauli formalism agree better with the ORCA-values. The deviation is reduced to about 15% and 35% for the Sn_2^{3+} and Pb_2^{3+} -molecule, respectively. The better agreement in case of the Pauli formalism, however, might be rather fortuitous. In case of the dimers, the influence of the SOC treatment is much larger than for the isolated ionized atoms, where it is almost negligible also for the heaviest atoms (cf. Table 1). Obvious the influence is not related to atomic SOC-properties, but related to the delicate interplay of the spins within the dimers. We thus attribute the difference between QE and ORCA values to the regime spin alignment introduced by our new scheme.

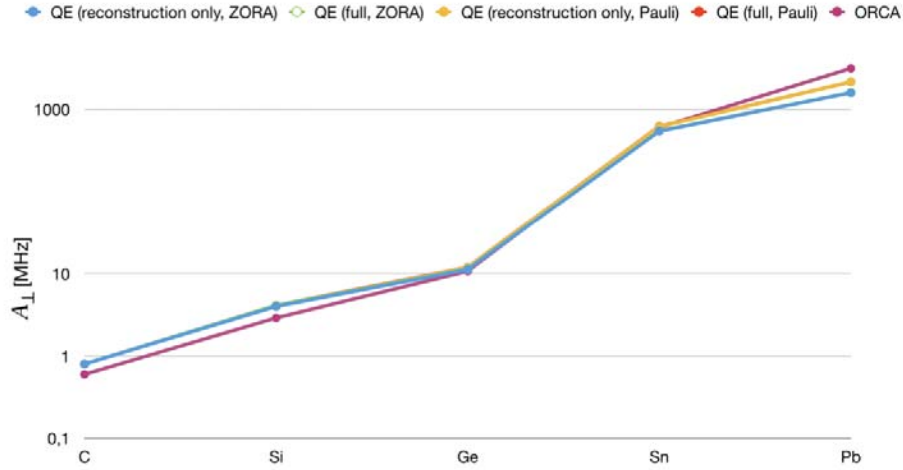


Figure 3. A^{orbital} for dimers of the Pb_2^{3+} -family

4. Crystalline systems

4.1. Ferromagnetic iron, bcc Fe

As a first crystalline system that is investigated with the new approach implemented in the QUANTUM ESPRESSO software package, the ferromagnetic ground state of iron, bcc Fe, is considered. As a ferromagnetic, i.e. metallic system, it provides a challenge for (double) perturbation theory, but is perfectly suited for a non-perturbative treatment based on the 'orbital magnetization' scheme.

In QE, this crystal is adequately simulated within a supercell approach (periodic boundary conditions, PBC). In order to take into account the system's metallic properties, the Brillouin zone of the reciprocal space is sampled by a dense $24 \times 24 \times 24 - \vec{k}$ -point mesh, whereby a cold (i.e. Marzari-Vanderbilt [19]) smearing is used. Within the GIPAW formalism, a plane-wave basis set with 200 Ry energy cut-off is used together with scalar relativistic norm-conserving pseudopotentials, whereby the ZORA formalism is employed to establish a SOC-including relativistic treatment as described in Section 2.1. As in Ref. [20] the same experimental (i.e. experimentally determined) lattice parameter of 2.856 nm is used [21], so that the resulting magnetic properties including the hyperfine splittings can be directly compared, and possible deviations can be attributed to differences in the method.

The system's orbital hyperfine tensor is characterized by only one value A^{orbital} due to its high symmetry (point group O_h). Based on this, the hyperfine splittings are often given in terms of the so-called hyperfine field $B^{\text{orbital}} = \frac{h}{g_I \mu_N} f^{\text{orbital}}$.

Table 4. Hyperfine fields $B^{\text{orbital}} = \frac{h}{g_I \mu_N} f^{\text{orbital}}$ and magnetic moments calculated with different DFT-based approaches. Available experimental data is also given.

	B^{orbital} [kG]	μ^{spin} [$\frac{\mu_B}{\text{cell}}$]	μ^{orbital} [$\frac{\mu_B}{\text{atom}}$]
LAPW (LSDA) [20]	26.0	2.278	0.048
LAPW (GGA)	24.1	2.275	0.045
LAPW + orbital polarization (LSDA) [20]	51.3		0.086
LAPW + orbital polarization (GGA) [20]	45.7		0.078
relativistic KKR [22]	24.6	2.136	0.056
fully relativistic KKR [23]	15.2	2.217	0.042
orbital magnetization scheme (this work)	34.0	2.255	0.065
experiment (from [24])	—	2.21	0.081

Table 4 lists calculated [20, 22, 23] and experimental data [24] from literature for the magnetic moments and the orbital hyperfine field B^{orbital} of bcc Fe whereby the experimental data is restricted to the magnetic moments, those of the spin as well as the orbital contribution. The herein presented calculation with the orbital magnetization scheme in QE yields $A^{\text{orb}} = 4.7$ MHz, i.e. an hyperfine field of $B^{\text{orbital}} = 34.0$ kG. The spin magnetic moment as calculated with QE as well as the reference values fairly agree with the experimental result, suggesting that all methods describe more or less the same ferromagnetic ground state.

The remaining difference between the values provided in Table 4 is expected to arise due to the different calculation schemes. The SOC is directly included in the SCF calculation in QE whereas Rodriguez et al. [20] included both, SOC and – as a correction to overcome the underestimation of the orbital magnetic moments – the so-called orbital polarization term via an additional variational approach. Ebert et al. [22, 23] calculated B^{orbital} with a relativistic Korringa-Kohn-Rostoker method. All of these schemes have in common, that the calculation of magnetic anisotropies is restricted to muffin-tin (MT) spheres around the nuclei, whereas our scheme take into account contributions from the interstitial regions [11]. Within the orbital magnetization scheme the QE-values are thus increased from a MT-derived standard PBE value around $0.04 \mu_B$ to $0.065 \mu_B$ per atom, which reaches fairly good agreement with the experimental value of $0.081 \mu_B$. The same behavior is found for the orbital hyperfine field. A value of 34.0 kG obtained with the present orbital magnetization-based approach may be better than those obtained by relativistic MT-based schemes (15 to 26 kG), but it is still considerably smaller than the orbital-polarization corrected scheme yielding values up to 52 KG. However, since there is no experimental reference data available for the orbital hyperfine field, it is not clear if and how much the values are overestimated by the semi-empirical orbital-polarisation corrected method [20].

4.2. Pb at MgO/Ag(111) substrate

We now turn our focus to a further ferromagnetic system, an individual Pb atom adsorbed at a MgO/Ag(111) surface. Similar systems, i.e Fe at the same metallic substrate [25] are frequently investigated in literature due to their potential use for spintronics application, e.g. for magnetic storage. DFT frequently leads to too small anisotropies in the magnetic properties such as hyperfine splittings, often attributed to limitations of DFT in general.

In this work, we investigate Pb adsorbed on MgO/Ag(111). More specifically we choose Pb at the oxygen adsorption site as a 2D periodic proof-of-principle system. The MgO/Ag(111) substrate was modelled starting from a orthorhombic unit cell (with 4.182 nm lateral lattice parameters) containing 6 Ag atoms, one Mg- and one O-atom [26]. After repeating (4×4) this unit cell in x and y -direction, we obtain a supercell containing in total 96 atoms, organized in 6 Ag layers and an isolating MgO layer on-top. The Brioullin zone of the 2D perodic system is sampled by a $4 \times 4 \times 1 - \vec{k}$ -point mesh, all other technical parameters are chosen identical to those used in case of Fe-bcc (previous section). The final structure is obtained by placing an Pb atom on top of an O atom. Afterwards the resulting structure has been optimized by relaxing all atoms, but those in the two lowest Ag layers, which are kept fix in order to mimic a transition to Ag bulk properties.

By this we were able to show that the nominally non-magnetic neutral Pb atom becomes spin-polarized with a spin magnetic moment of $1.95 \mu_B$ and large values for the orbital magnetic moment, $-0.65 \mu_B$ in-plane and almost atom-like $-1.80 \mu_B$ out-of-plane, already suggesting that orbital quenching might be efficiently suppressed by the presence of the substrate. In fact, by applying the present orbital magnetization scheme for calculating the orbital contribution to the hyperfine splitting, we obtained a quite large dipolar splitting of about 851 MHz, but actually a huge orbital splitting of 4189 MHz. With a factor of 4.92 this nearly perfectly reflects the 5:1 ratio rule derived for $p_{3/2}$ electrons, finally proving that orbital quenching is almost completely suppressed.

5. Summary

In this work, a novel, basically non-perturbative scheme for the calculation of the orbital part of the hyperfine tensor has been derived, implemented in the Quantum ESPRESSO (QE) code, and carefully evaluated. For molecular systems we found excellent matching between A^{orbital} as calculated with the new scheme and those obtained by double perturbation theory (ORCA code). For isolated atoms we analytically derive relativistic ratio rules for the orbital and dipolar contribution to the hyperfine splittings of spherically symmetric one-electron systems. The predicted angular-momentum (j)-depending integer values are perfectly reflected if applying the new scheme to ionized isolated atoms of the Pb^+ family. Here the spin density is given by an unpaired electron in a $p_{3/2}$ orbital characterized with $A^{\text{orbital}} = 5 \cdot A^{\text{dipolar}}$, whereby the absolute value of the orbital part scales with the strength of spin-orbit coupling (SOC), contributing huge values in the GHz range to the energy splittings of the hyperfine structure.

Thanks to the underlying supercell approach the new method is also applicable to 3D and 2D periodic systems. In case of bcc Fe the orbital part of the hyperfine field as calcu-

lated with QE appear to be superior to relativistic schemes using the muffin-tin approximation, approaching the values predicted by empirically corrected schemes. By applying the new scheme onto a non-magnetic neutral Pb atom adsorbed on a metallic MgO/Ag(111) substrate, it is shown that the 5:1 ratio rules derived for $p_{3/2}$ electrons also holds in this case. We thus argue that recent reports of DFT failing in HFI-prediction for similar systems could be attributed to the fact that the orbital term has been neglected. The derived j -depending ratio rules with integer values up to 3, 5, and 9, for p , d , and f electrons, respectively, define the maximum orbital hyperfine values and nicely demonstrate the importance of the orbital contribution for quasi-atomic single-orbital states, e.g. for single atoms at surfaces, where orbital quenching is hindered by low local symmetry.

Acknowledgements

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Appendix A. Analytical treatment of the hyperfine splitting

This section gives additional relevant background information on the solution of Dirac's Equation in a fully relativistic, four-component manner for single-electron problems and on the analytical treatment of the hyperfine splitting for hydrogen-like atoms, i.e. single electrons in spherically symmetric potentials $V(r)$. In order to solve the corresponding Dirac's equation

$$[c\vec{\alpha} \cdot \vec{p} + \beta mc^2 + V(r)]\Psi^{\text{rel}} = E\Psi^{\text{rel}} \quad (\text{A.1})$$

the following product approach for the wave function $\Psi^{\text{rel}}(\vec{r}) = \begin{bmatrix} \psi_L \\ \psi_S \end{bmatrix}$ is expedient [13]

$$\begin{aligned} \psi_L &= g(r)\Omega_{1,j,l,m_j} \\ \psi_S &= if(r)\Omega_{2,j,l,m_j}. \end{aligned} \quad (\text{A.2})$$

Thus, both components of Ψ^{rel} consist of two-dimensional, relativistic spherical harmonics and radial wave functions [13].

The relativistic spherical harmonics in Equation A.2 are given by

$$\Omega_{1,j,l,m_j} = \begin{bmatrix} N_1 Y_{l,m_j-\frac{1}{2}}(\vartheta, \varphi) \\ N_2 Y_{l,m_j+\frac{1}{2}}(\vartheta, \varphi) \end{bmatrix} \quad \text{and} \quad \Omega_{2,j,l,m_j} = \begin{bmatrix} N_3 Y_{\tilde{l},m_j-\frac{1}{2}}(\vartheta, \varphi) \\ N_4 Y_{\tilde{l},m_j+\frac{1}{2}}(\vartheta, \varphi) \end{bmatrix}.$$

Here,

$$Y_{l,m}(\vartheta, \varphi) = \frac{1}{\sqrt{2\pi}} N_{l,m} e^{im\varphi} P_l^{|m|}(\cos(\vartheta))$$

denote the spherical harmonics with the associated Legendre polynomials $P_{l,m}$,

$$N_{l,m} = \epsilon \sqrt{\frac{2l+1}{2} \frac{(l-|m|)!}{(l+|m|)!}} \quad (\text{A.3})$$

and

$$\epsilon = \begin{cases} (-1)^m, & \text{if } m \geq 0 \\ 1, & \text{if } m < 0 \end{cases}. \quad (\text{A.4})$$

Table A1. Prefactors N_i of the spherical harmonics contributing to the relativistic spherical harmonics.

j	$\tilde{l}$	N_1	N_2	N_3	N_4
$l + s$	$l + 1$	$\sqrt{\frac{l+m_j+\frac{1}{2}}{2l+1}}$	$-\sqrt{\frac{l-m_j+\frac{1}{2}}{2l+1}}$	$\sqrt{\frac{l-m_j+\frac{3}{2}}{2l+3}}$	$\sqrt{\frac{l+m_j+\frac{3}{2}}{2l+3}}$
$l - s$	$l - 1$	$\sqrt{\frac{l-m_j+\frac{1}{2}}{2l+1}}$	$\sqrt{\frac{l+m_j+\frac{1}{2}}{2l+1}}$	$\sqrt{\frac{l+m_j-\frac{1}{2}}{2l-1}}$	$-\sqrt{\frac{l-m_j-\frac{1}{2}}{2l-1}}$

The prefactors N_1 , N_2 , N_3 and N_4 are given in Table A1. The radial wave functions $f(r)$ and $g(r)$ are solutions of a system of coupled equations that arises from inserting ansatz A.2 in Equation A.1 and depend on the form of the potential. Thereby, the solutions to Equation A.1 can be classified by the quantum numbers n , l , j and m_j .

According to Blügel et al. [3], the energy correction due to the hyperfine splitting according to Equation 1 for a radialsymmetric potential V consists of three terms:

$$\Delta E_{\text{hyperfine}} = \Delta E_{\text{orbital}} + \Delta E_{\text{dipolar}} + \Delta E_{\text{contact}}$$

with

$$\begin{aligned} \Delta E_{\text{orbital}} &= -\frac{e}{m} \frac{\mu_0}{4\pi} \vec{\mu}_I \cdot \langle \Psi_L | \frac{S(r)}{r^3} \hat{L} | \Psi_L \rangle \\ \Delta E_{\text{dipolar}} &= \frac{e\hbar}{2m} \frac{\mu_0}{4\pi} \langle \Psi_L | \frac{S(r)}{r^3} [\hat{\sigma} \cdot \vec{\mu}_I - 3(\hat{\sigma} \cdot \vec{e}_r)(\vec{\mu}_I \cdot \vec{e}_r)] | \Psi_L \rangle \\ \Delta E_{\text{contact}} &= -\frac{8\pi}{3} \frac{e\hbar}{2m} \frac{\mu_0}{4\pi} \langle \Psi_L | S(r) \hat{\sigma} \vec{\mu}_I \cdot \delta(\vec{r}) | \Psi_L \rangle - \frac{e\hbar}{2m} \frac{\mu_0}{4\pi} \langle \Psi_L | \frac{1}{r^2} \frac{\partial S}{\partial r} [\hat{\sigma} \cdot \vec{\mu}_I - (\hat{\sigma} \cdot \vec{e}_r)(\vec{\mu}_I \cdot \vec{e}_r)] | \Psi_L \rangle \end{aligned} \quad (\text{A.5})$$

Using the ansatz Eq. A.2, these hyperfine splitting energies can be calculated as a sum of the following three contributions if hydrogen-like atoms are considered:

$$\begin{aligned} \Delta E_{\text{orbital}} &= -\frac{e\hbar}{m} \frac{\mu_0}{4\pi} \mu_{I,z} \beta_{\text{orbital}} \int_0^\infty \frac{S(r)}{r} |g(r)|^2 dr, \\ \Delta E_{\text{dipolar}} &= \frac{1}{2} \frac{e\hbar}{m} \frac{\mu_0}{4\pi} \mu_{I,z} \beta_{\text{dipolar}} \int_0^\infty \frac{S(r)}{r} |g(r)|^2 dr, \\ \Delta E_{\text{contact}} &= \Delta E_{\text{contact},\delta} + \Delta \bar{E}_{\text{contact}} \quad \text{with:} \\ \Delta E_{\text{contact},\delta} &= -\frac{4}{3} \frac{e\hbar}{2m} \frac{\mu_0}{4\pi} \mu_{I,z} \beta_{\text{contact},\delta} \int_0^\infty |g(r)|^2 S(r) \delta(r) dr \\ \text{and} \\ \Delta \bar{E}_{\text{contact}} &= -\frac{e\hbar}{2m} \frac{\mu_0}{4\pi} \mu_{I,z} \beta_{\text{contact}} \int_0^\infty \frac{\partial S}{\partial r} |g(r)|^2 dr. \end{aligned} \quad (\text{A.6})$$

The angular integrals β in Equation A.6 are given by:

$$\begin{aligned}
\beta_{\text{orbital}} &= (m_j - \frac{1}{2})N_1^2 + (m_j + \frac{1}{2})N_2^2 \\
\beta_{\text{dipolar}} &= N_1^2 - N_2^2 - 3N_1^2N_{l,m_j-\frac{1}{2}}^2 \int_{-1}^1 P_{l,|m_j-\frac{1}{2}|}(x)^2 x^2 dx + 3N_2^2N_{l,m_j+\frac{1}{2}}^2 \int_{-1}^1 P_{l,|m_j+\frac{1}{2}|}(x)^2 x^2 dx \\
&\quad - 6N_1N_2N_{l,m_j-\frac{1}{2}}N_{l,m_j+\frac{1}{2}} \int_{-1}^1 P_{l,|m_j-\frac{1}{2}|}(x)P_{l,|m_j+\frac{1}{2}|}(x)x\sqrt{1-x^2}dx \\
\beta_{\text{contact},\delta} &= N_1^2N_{l,m_j-\frac{1}{2}}\delta_{m_j,\frac{1}{2}} - N_2^2N_{l,m_j+\frac{1}{2}}\delta_{m_j,-\frac{1}{2}} \\
\beta_{\text{contact}} &= N_1^2 - N_2^2 - N_1^2N_{l,m_j-\frac{1}{2}}^2 \int_{-1}^1 P_{l,|m_j-\frac{1}{2}|}(x)^2 x^2 dx + N_2^2N_{l,m_j+\frac{1}{2}}^2 \int_{-1}^1 P_{l,|m_j+\frac{1}{2}|}(x)^2 x^2 dx \\
&\quad - 2N_1N_2N_{l,m_j-\frac{1}{2}}N_{l,m_j+\frac{1}{2}} \int_{-1}^1 P_{l,|m_j-\frac{1}{2}|}(x)P_{l,|m_j+\frac{1}{2}|}(x)x\sqrt{1-x^2}dx. \tag{A.7}
\end{aligned}$$

An evaluation of the angular parts of these hyperfine splitting integrals allows the conclusion of identities, which come in handy for the evaluation of quasi-atomic problems, where the spin density is localized in a single atom-like orbital. For all single-electron states, ratio rules between orbital and dipolar hyperfine splitting may be deduced, depending on the angular momentum quantum numbers l and j .

In case of a $p_{\frac{1}{2}}$ state (i.e. $l = 1, j = \frac{1}{2}, m_j = \pm\frac{1}{2}$), A.7 leads to $\beta_{\text{orbital}} = -\frac{1}{2}\beta_{\text{dipolar}}$ and with the similarity of $\Delta E_{\text{orbital}}$ and $\Delta E_{\text{dipolar}}$ in Equation A.6, $\Delta E_{\text{orbital}}(p_{\frac{1}{2}}, m_j = \pm\frac{1}{2}) = \Delta E_{\text{dipolar}}(p_{\frac{1}{2}}, m_j = \pm\frac{1}{2})$ can be concluded, leading to a 1:1 ratio rule:

$$\begin{aligned}
f_{\text{orbital}}(p_{\frac{1}{2}}) &= \frac{\Delta E_{\text{orbital}}(p_{\frac{1}{2}}, m_j = -\frac{1}{2}) - \Delta E_{\text{orbital}}(p_{\frac{1}{2}}, m_j = \frac{1}{2})}{\hbar} \\
&= \frac{\Delta E_{\text{dipolar}}(p_{\frac{1}{2}}, m_j = -\frac{1}{2}) - \Delta E_{\text{dipolar}}(p_{\frac{1}{2}}, m_j = \frac{1}{2})}{\hbar} \\
&= f_{\text{dipolar}}(p_{\frac{1}{2}}). \tag{A.8}
\end{aligned}$$

For a $p_{\frac{3}{2}}$ state (i.e. $l = 1, j = \frac{3}{2}, m_j = \pm\frac{3}{2}$ or $m_j = \pm\frac{1}{2}$), A.7 leads to $\beta_{\text{orbital}} = \frac{1}{10}\beta_{\text{dipolar}}$. Thus, Equation A.6 allows the conclusion of $\Delta E_{\text{orbital}}(p_{\frac{3}{2}}, m_j = \pm\frac{3}{2}/\pm\frac{1}{2}) = -5\Delta E_{\text{dipolar}}(p_{\frac{1}{2}}, m_j = \pm\frac{3}{2}/\pm\frac{1}{2})$, which leads to 5:1 ratio rules:

$$\begin{aligned}
f_{\text{orbital}}(p_{\frac{3}{2}}) &= \frac{\Delta E_{\text{orbital}}(p_{\frac{3}{2}}, m_j = -\frac{3}{2}/-\frac{1}{2}) - \Delta E_{\text{orbital}}(p_{\frac{3}{2}}, m_j = \frac{3}{2}/\frac{1}{2})}{\hbar} \\
&= \frac{-5\Delta E_{\text{dipolar}}(p_{\frac{3}{2}}, m_j = -\frac{3}{2}/-\frac{1}{2}) + 5\Delta E_{\text{dipolar}}(p_{\frac{1}{2}}, m_j = \frac{3}{2}/\frac{1}{2})}{\hbar} \\
&= -5 \cdot f_{\text{dipolar}}(p_{\frac{3}{2}}). \tag{A.9}
\end{aligned}$$

Notably, these ratio rules do not depend on the principal quantum number n , and can also be derived for higher angular momentum numbers, i.e. d and f electrons (see Table A2).

Table A2. ratios $\eta = \frac{\Delta E_{\text{orb}}}{\Delta E_{\text{dip}}}$ for p , d , and f states

l	j	m_j	β_{orb}	β_{dip}	$\eta = -2\frac{\beta_{\text{orb}}}{\beta_{\text{dip}}} = \frac{\Delta E_{\text{orb}}}{\Delta E_{\text{dip}}}$
1	$\frac{1}{2}$	$\pm\frac{1}{2}$	$\pm\frac{2}{3}$	$\mp\frac{4}{3}$	1
		$\pm\frac{1}{2}$	$\pm\frac{1}{3}$	$\pm\frac{2}{15}$	-5
		$\pm\frac{3}{2}$	± 1	$\pm\frac{2}{5}$	-5
2	$\frac{3}{2}$	$\pm\frac{1}{2}$	$\pm\frac{3}{5}$	$\mp\frac{2}{5}$	3
		$\pm\frac{3}{2}$	$\pm\frac{9}{5}$	$\mp\frac{6}{5}$	3
		$\pm\frac{5}{2}$	$\pm\frac{3}{5}$	$\pm\frac{4}{35}$	-7
	$\frac{5}{2}$	$\pm\frac{3}{2}$	$\pm\frac{6}{5}$	$\pm\frac{12}{35}$	-7
		$\pm\frac{5}{2}$	$\pm\frac{2}{5}$	$\pm\frac{4}{35}$	-7
		$\pm\frac{7}{2}$	± 2	$\pm\frac{4}{7}$	-7
3	$\frac{5}{2}$	$\pm\frac{1}{2}$	$\pm\frac{4}{7}$	$\mp\frac{8}{35}$	5
		$\pm\frac{3}{2}$	$\pm\frac{12}{7}$	$\mp\frac{24}{35}$	5
		$\pm\frac{5}{2}$	$\pm\frac{20}{7}$	$\mp\frac{8}{35}$	5
	$\frac{7}{2}$	$\pm\frac{1}{2}$	$\pm\frac{3}{7}$	$\pm\frac{2}{21}$	-9
		$\pm\frac{3}{2}$	$\pm\frac{9}{7}$	$\pm\frac{2}{21}$	-9
		$\pm\frac{5}{2}$	$\pm\frac{15}{7}$	$\pm\frac{10}{21}$	-9
		$\pm\frac{7}{2}$	± 3	$\pm\frac{2}{3}$	-9
		$\pm\frac{9}{2}$	± 3	$\pm\frac{2}{3}$	-9
		$\pm\frac{11}{2}$	± 3	$\pm\frac{2}{3}$	-9

The information included in Table A2 can be summarized by the following j -dependent ratio rules:

$$\eta = \frac{\Delta E_{\text{orbital}}}{\Delta E_{\text{dipolar}}} = -2\frac{\beta_{\text{orbital}}}{\beta_{\text{dipolar}}} = \begin{cases} 2j & \text{for } j = l - 1/2 \\ -2(j+1) & \text{for } j = l + 1/2 \end{cases} \tag{A.10}$$

Appendix B. Results and further details of calculations with ORCA and QE

This appendix lists the full set of calculated hyperfine tensors for all investigated molecular systems as well as the bond length (as calculated with ORCA) used for all calculations,

ensuring that both simulations schemes (QE as well as ORCA) describe the same electronic state. Table B11 summarizes the atomic mass and the nuclear g_N -factor of the isotopes for which the hyperfine tensors have been calculated.

The molecules' simulation in ORCA uses the PBE-functional and a scalar relativistic ZORA formalism as well as the SARC-ZORA-TZVP basis set (for I, Sn and Pb). For all other atoms the ZORA-def-2-TZVP basis set has been used. In QE, the PBE-functional, a cubic cell with edge length of $a = 25 r_B$, a cut-off energy of $E_{\text{cut-off}} = 80$ Ry (or $E_{\text{cut-off}} = 100$ Ry in case of the Fe- and FeI-type molecules) and a $1 \times 1 \times 1$ Γ -centered $\vec{k}$ -point grid are used in order to mimic isolated finite systems. Besides the ZORA formalism, the Pauli formalism is used. In the relaxation as well as in the hyperfine calculation, the z -axis is chosen as the C_∞ -axis of the molecules. The investigated tensors are diagonal and consist of a value orthogonal ($A_\perp$) and one parallel ($A_\parallel$) to this symmetry axis.

Table B1. The tables where the hyperfine tensors are registered are listed.

molecules	bond length	A^{dipolar}	A^{orbital}
Diatomic radicals	B2	B3	B4
Pb_2^{3+} -family	B5	B6	B7
FeI-type molecules	B8	B9	B10

Table B2. Bond length used for modelling the molecular systems from Ref. [18]

Molecule	bond length in Å	Molecule	bond length in Å	Molecule	bond length in Å
NF	1.327	CrN	1.538	S ₂	1.912
O ₂	1.219	Ge ₂ ⁺	2.158	AsF	1.77
PF	1.619	Sn ₂ ⁺	2.532	Si ₂ ⁺	2.065
SO	1.506	CrH	1.643	Si ₂ ⁺	2.065
SH ⁺	1.383	MnO	1.619	V ₂ ⁺	1.697
VO	1.583	MnS	2.034	CrF	1.78

Table B3. A^{dipolar} for molecules from Ref. [18] with spin $S = 1$, $S = \frac{3}{2}$ and $S = \frac{5}{2}$ (top, middle and bottom table, respectively)

Molecule	atom	$A_{\perp}^{\text{dip}}$ in MHz		$A_{\parallel}^{\text{dip}}$ in MHz	
		ORCA	QE	ORCA	QE
NF	N	23.2	25.1	-46.5	-50.1
	F	151.0	138.9	-301.9	-277.7
O ₂	O	-44.6	-46.6	89.1	93.2
PF	P	157.9	170.1	-315.7	-340.2
	F	87.7	76.8	-175.4	-153.7
SO	S	30.1	32.0	-60.1	-63.9
	O	-31.5	-32.6	62.9	65.3
SH	S	49.5	52.6	-98.9	-105.3
	H	-11.3	-11.3	22.6	22.6
S ₂	S	24.8	26.1	-49.6	-52.3
AsF	As	146.9	157.8	-293.8	-315.6
	F	85.3	75.6	-170.6	-151.1

Molecule	atom	$A_{\perp}^{\text{dip}}$ in MHz		$A_{\parallel}^{\text{dip}}$ in MHz	
		ORCA	QE	ORCA	QE
Si ₂ ⁺	Si	6.0	5.9	-11.9	-11.9
VO	V	47.6	51.8	-95.3	-103.7
	O	2.7	2.5	-5.5	-5.1
V ₂ ⁺	V	24.3	31.6	-48.6	-63.2
CrN	Cr	-11.9	-12.3	23.8	24.6
	N	-3.4	-2.8	4.9	5.5
Ge ₂ ⁺	Ge	2.5	2.7	-5.0	-5.4
Sn ₂ ⁺	Sn	38.7	37.9	-77.5	-75.7

Molecule	atom	$A_{\perp}^{\text{dip}}$ in MHz		$A_{\parallel}^{\text{dip}}$ in MHz	
		ORCA	QE	ORCA	QE
CrH	Cr	-1.8	-1.6	3.6	3.1
	H	-14.2	-14.3	28.5	28.5
CrF	Cr	-3.0	-2.8	6.0	5.6
	F	27.1	25.7	-54.2	-51.4
MnO	Mn	25.8	30.0	-51.6	-60.1
	O	-8.4	-8.7	16.7	17.3
MnS	Mn	17.1	14.7	-34.2	-29.3
	S	6.4	6.6	-12.8	-13.1

Table B4. A^{orbital} for molecules from Ref. [18] with spin $S = 1$, $S = \frac{3}{2}$ and $S = \frac{5}{2}$ (top, middle and bottom table, respectively)

Molecule	atom	$A_{\perp}^{\text{orb}}$ in MHz			$A_{\parallel}^{\text{orb}}$ in MHz		
		ORCA	QE (rec.)	QE (full)	ORCA	QE(rec.)	QE(full)
NF	N	0.1	0.1	0.1	-0.2	-0.2	-0.2
	F	0.7	1.8	1.7	1.7	3.2	3.0
O ₂	O	-0.2	-0.6	-0.6	0.4	0.2	0.2
PF	P	-1.4	-3.4	-3.5	0.6	-5.1	-5.2
	F	6.2	6.8	6.7	-0.8	0.1	0.1
SO	S	0.3	0.0	0.0	0.5	-0.4	-0.4
	O	-1.4	-1.8	-1.8	1.4	1.3	1.3
SH	S	1.5	0.9	1.0	0.0	-1.5	-1.5
	H	0.1	0.0	0.1	0.0	0.0	0.0
S ₂	S	1.4	1.2	1.2	-0.1	-0.9	-0.9
AsF	As	-35.8	-27.9	-27.9	-32.8	-22.1	-22.1
	F	40.7	37.5	37.2	-12.1	-11.0	-10.8

Molecule	atom	$A_{\perp}^{\text{orb}}$ in MHz			$A_{\parallel}^{\text{orb}}$ in MHz		
		ORCA	QE (rec.)	QE(full)	ORCA	QE (rec.)	QE(full)
Si ₂ ⁺	Si	0.9	1.6	1.6	-0.1	0.5	0.5
VO	V	-6.7	-8.0	-8.6	-3.0	-3.6	-3.8
	O	0.0	0.2	0.1	0.0	0.0	0.0
V ₂ ⁺	V	-1.9	-2.3	-2.5	-1.5	-1.7	-1.9
CrN	Cr	1.1	1.3	1.4	0.9	1.1	1.1
	N	0.0	0.0	0.0	0.0	0.1	0.1
Ge ₂ ⁺	Ge	4.2	5.0	5.0	1.2	1.7	1.7
Sn ₂ ⁺	Sn	259.7	230.4	230.9	97.1	89.3	89.3

Molecule	atom	$A_{\perp}^{\text{orb}}$ in MHz			$A_{\parallel}^{\text{orb}}$ in MHz		
		ORCA	QE (rec.)	QE(full)	ORCA	QE (rec.)	QE(full)
CrH	Cr	1.0	1.1	1.2	0.7	0.7	0.7
	H	0.1	0.0	0.3	0.0	0.0	0.0
CrF	Cr	1.7	1.9	2.0	0.7	0.7	0.7
	F	4.0	4.2	4.3	0.6	0.5	0.5
MnO	Mn	-6.1	-2.7	-2.8	-4.0	-1.5	-1.6
	O	-1.3	-1.4	-1.5	0.0	0.0	0.0
MnS	Mn	-1.3	-2.6	-2.6	-4.3	-5.6	-5.9
	S	0.4	0.4	0.4	0.2	0.0	0.0

Table B5. bond length for dimers of the Pb_2^{2+} family (the bond length for the dimers of the Pb_2^{2+} -family are used for the calculations of the hyperfine tensors of the Pb_2^{3+} -family, because the representatives of the latter group tend to dissociate in a relaxation calculation)

Dimer	bond length in Å	Dimer	bond length in Å
C_2^{2+}	1.900	Sn_2^{2+}	3.070
Si_2^{2+}	2.402	Pb_2^{2+}	3.604
Ge_2^{2+}	2.667		

Table B6. A^{dipolar} for dimers of the Pb_2^{3+} -family

Dimer	$A_{\perp}^{\text{dipolar}}$ in MHz			$A_{\parallel}^{\text{dipolar}}$ in MHz		
	ORCA		QE	ORCA		QE
	ZORA	Pauli		ZORA	Pauli	
C_2^{3+}	-59.2	-62.6	-62.6	118.4	125.2	125.2
Si_2^{3+}	68.8	71.1	71.1	-137.6	-142.2	-142.2
Ge_2^{3+}	29.2	30.2	30.2	-58.4	-60.3	-60.3
Sn_2^{3+}	483.3	481.9	481.9	-966.7	-963.7	-963.7
Pb_2^{3+}	-529.3	-536.9	-537.8	1058.7	1073.7	1075.7

Table B7. A^{orbital} for dimers of the Pb_2^{3+} -family.

dimer	$A_{\perp}^{\text{orbital}}$ [MHz]					$A_{\parallel}^{\text{orbital}}$ [MHz]	
	ORCA	QE (rec.)		QE (full)		ORCA	QE (rec/full) ZORA/Pauli
		ZORA	Pauli	ZORA	Pauli		
C_2^{3+}	-0.6	-0.8	-0.8	-0.8	-0.8	0.0	0.0
Si_2^{3+}	2.9	4.0	4.0	4.1	4.1	0.0	0.0
Ge_2^{3+}	10.7	11.2	11.8	11.4	11.9	0.1	0.0
Sn_2^{3+}	600.2	542.1	615.8	546.4	620.8	3.3	0.0
Pb_2^{3+}	-3126.7	-1586.8	-2140.1	-1590.4	-2141.9	-8.1	0.0

Table B8. bond length for Fe- and FeI-type molecules (the FeI_2^+ -molecule is linear, the distance between the outer I atoms is $d = 5.212 \text{ \AA}$)

molecule	bond length in $\text{\AA}$	S
Fe_2^+	1.944	$\frac{5}{2}$
FeI	2.530	$\frac{5}{2}$
FeI^+	2.534	3
FeI_2^+	5.212	$\frac{5}{2}$

Table B9. A^{dipolar} for Fe- and FeI-type molecules

Molecule	atom	$A_{\perp}^{\text{dip}}$ in MHz		$A_{\parallel}^{\text{dip}}$ in MHz	
		ORCA	QE	ORCA	QE
Fe_2^+	Fe	4.5	4.4	-9.0	-8.8
FeI	Fe	-5.0	-4.1	10.0	8.2
	I	-8.2	-8.4	16.5	16.8
FeI^+	Fe	1.1	2.1	-2.3	-4.2
	I	29.0	29.6	-58.0	-59.2
FeI_2^+	Fe	2.6	3.3	-5.3	-6.6
	I	55.0	51.4	-110.1	-102.9

Table B10. A^{orbital} for Fe- and FeI-type molecules

Molecule	atom	$A_{\perp}^{\text{orb}}$ in MHz			$A_{\parallel}^{\text{orb}}$ in MHz		
		ORCA	QE (rec.)	QE (full)	ORCA	QE (rec.)	QE (full)
Fe_2^+	Fe	1.5	2.2	2.3	3.5	4.4	4.7
FeI	Fe	3.3	4.0	4.2	2.2	3.8	4.0
	I	14.7	13.3	11.9	32.9	19.3	19.5
FeI^+	Fe	5.4	5.9	6.2	-7.2	-5.8	-6.2
	I	46.6	42.2	42.3	132.4	106.7	107.0
FeI_2^+	Fe	6.2	6.6	7.0	-7.0	-6.0	-6.3
	I	-5.4	-1.9	-1.9	45.7	43.4	43.5

Table B11. atomic mass and nuclear g_N -value from [27] for the nuclei for which the hyperfine interaction has been calculated

atom	atomic mass	nuclear g_N -value
^1H	1.008	5.58569468
^7Li	6.94	0.8220473
^{13}C	12.011	1.404824
^{14}N	14.067	0.40376100
^{17}O	15.999	-0.757516
^{19}F	18.998	5.253736
^{29}Si	28.085	-1.11058
^{31}P	30.974	2.2632
^{33}S	32.06	0.429214
^{51}V	50.942	1.4710588
^{53}Cr	51.996	-0.31636
^{55}Mn	54.938	1.38748716
^{57}Fe	55.847	0.181246
^{73}Ge	72.630	-0.1954373
^{75}As	74.992	0.959647
^{119}Sn	118.71	-2.09456
^{127}I	126.9	1.12531
^{207}Pb	207.2	1.1644