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Relativistic nuclear magnetic resonance chemical shifts of heavy nuclei with pseudopotentials and the zeroth-order regular approximation

Jonathan R. Yates,[a] Chris J. Pickard, and Mike C. Payne
TCM Group, Cavendish Laboratory, Madingley Road, Cambridge CB3 OHE, United Kingdom

Francesco Mauri
Laboratoire de Minéralogie-Cristallographie de Paris, Université Pierre et Marie Curie, 4 Place Jussieu, 75252, Paris, Cedex 05, France

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We present a method for the first principles density functional calculation of relativistic all-electron nuclear magnetic resonance chemical shifts using pseudopotentials. The method is based on the gauge including projector augmented wave approach of Pickard and Mauri [Phys. Rev. B **63**, 245101 (2001)]. Relativistic effects are included at the level of the scalar-relativistic zeroth-order regular approximation. The method allows chemical shifts of large, low symmetry structures containing heavy elements to be calculated efficiently. We demonstrate its success for a range of Se and Te containing molecules.
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I. INTRODUCTION

Nuclear magnetic resonance (NMR) experiments on heavy nuclei present both experimental and theoretical challenges. As measurements of the chemical shift of nuclei beyond the second period are becoming increasingly common, it is important that accurate theoretical techniques are available to predict and interpret these experimental results. First principles density functional (DFT) calculations have been shown to provide an excellent description of the chemical shieldings for compounds containing light elements.[1] However, the extension to higher atomic numbers poses two distinct challenges; first dealing with the large number of electrons which must be explicitly considered and second, accounting for the effects of special relativity.

Relativity strongly affects NMR shielding parameters as these parameters are dominated by the region of space near to the nucleus. In this region the electrons experience the strong nuclear potential and have a large local momentum. This is true for both the valence electrons as well as the tightly bound core electrons.

Fully relativistic calculations, based on a four-component Hamiltonian, are time consuming and, at the present time, limited to small systems.[2] Various two-component formalisms have been developed and one of the most simple and elegant is the zeroth-order regular approximation (ZORA).[3–5]

Regardless of the method employed, all-electron calculations on systems containing heavy elements will be computationally demanding due to the large number of electrons. A more computationally attractive solution would be to use pseudopotentials, which treat only the valence electrons fully. Pseudopotentials are most commonly employed within a frozen core approximation however, in principle this condition can be relaxed.[6] Kaupp *et al.*[7,8] have used pseudopotentials to represent the core electrons of a transition metal atom in various complexes. This allows for the efficient calculation of the chemical shielding of the light elements in the system. It has been shown[9] that the contribution to the chemical shift from the core electrons is rigid and so the calculation of the shielding of the heavy atom itself is possible. However, this poses a significant problem as the pseudo-wave-function differs significantly from the all-electron wave function in the core region.

Recently, Pickard and Mauri[10] have presented a gauge including extension to Blöchl's projector augmented wave (PAW)[11] method which allows for the calculation of all-electron NMR chemical shifts with pseudopotentials. This allows the use of pseudopotentials for all atoms in the system to obtain maximal computational advantage.

In this paper we show that this gauge including projector augmented wave (GIPAW) approach provides a natural framework for the inclusion of relativistic effects in core properties such as chemical shifts. The relativistic nature of the valence electrons close to the core is of paramount importance and we derive relativistic GIPAW operators that take this into account.

II. THEORY

A. Introduction

We begin by reviewing the zeroth-order regular approximation to the Dirac equation. We then discuss Blöchl's PAW scheme and show how it may be used to calculate all-electron observables from a pseudopotential calculation. Using a gauge invariant extension to PAW we derive a pseudo-Hamiltonian and pseudocurrent operator from the ZORA Hamiltonian and show how scalar relativistic all-electron chemical shifts can be obtained from pseudopotential calculations.

B. Zeroth-order regular approximation

We start with the time-independent single particle Dirac equation for an electron in external magnetic field, **B**;

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[a] Electronic mail: jry20@phy.cam.ac.uk

$$\begin{pmatrix} V(\mathbf{r}) & c\boldsymbol{\sigma}\cdot\boldsymbol{\pi} \\ c\boldsymbol{\sigma}\cdot\boldsymbol{\pi} & V(\mathbf{r})-2c^2 \end{pmatrix}\begin{pmatrix} |\Phi\rangle \\ |\chi\rangle \end{pmatrix}=E\begin{pmatrix} |\Phi\rangle \\ |\chi\rangle \end{pmatrix}, \tag{1}$$

where $\boldsymbol{\sigma}$ are the Pauli matrices and c is the speed of light. The canonical momentum, $\boldsymbol{\pi}$, is given by $\boldsymbol{\pi}=\mathbf{p}+(1/c)\mathbf{A}(\mathbf{r})$ where $\mathbf{B}=\boldsymbol{\nabla}\times\mathbf{A}(\mathbf{r})$. Within density functional theory $V(\mathbf{r})$ is the effective Kohn–Sham potential given by the sum of the nuclear, Hartree, and exchange-correlation potentials. The Dirac wave function has two spinor components, $|\Phi\rangle$ and $|\chi\rangle$, called the large and small component, respectively. The large and small components are related by $|\chi\rangle=X|\Phi\rangle$, where

$$X=\frac{1}{2c}\left(1+\frac{E-V(\mathbf{r})}{2c^2}\right)^{-1}\boldsymbol{\sigma}\cdot\boldsymbol{\pi}. \tag{2}$$

It is therefore possible to express the Dirac equation in terms of the large component only,

$$(V(\mathbf{r})+c\,\boldsymbol{\sigma}\cdot\boldsymbol{\pi}X)|\Phi\rangle=E|\Phi\rangle. \tag{3}$$

The large component $|\Phi\rangle$ is not normalized. We introduce a normalized two-component wave function $|\Psi\rangle$ given by

$$|\Psi\rangle=(\sqrt{1+X^{\dagger}X})|\Phi\rangle. \tag{4}$$

Traditionally Eq. (3) is simplified by assuming that $p^2 \ll 4c^2$, which leads to the relativistic Pauli approximation. However, for a divergent potential such as a Coulomb potential there will exist a region, close to the nucleus, in which an expansion based on the Pauli assumption is not valid. The size, and hence importance, of this region will increase with atomic number. To avoid this problem we follow the approach of van Lenthe[3] and rewrite Eq. (2) as

$$X=\left(\frac{c}{2c^2-V(\mathbf{r})}\right)\left(1+\frac{E}{2c^2-V(\mathbf{r})}\right)^{-1}\boldsymbol{\sigma}\cdot\boldsymbol{\pi}. \tag{5}$$

If we assume that $E\ll(2c^2-V(\mathbf{r}))$ and expand to zeroth order in $E/(2c^2-V(\mathbf{r}))$ we obtain the so-called zeroth-order regular approximation (ZORA). The assumption that $E\ll(2c^2-V(\mathbf{r}))$ remains valid close to the nucleus, where the Coulomb potential is divergent. It can be shown that ZORA will be more accurate for low energy valence electrons than deep core states as a result of the approximations made.[12] The ZORA Hamiltonian is

$$H_{\text{ZORA}}=\boldsymbol{\sigma}\cdot\boldsymbol{\pi}\frac{K(\mathbf{r})}{2}\boldsymbol{\sigma}\cdot\boldsymbol{\pi}+V(\mathbf{r}), \tag{6}$$

where

$$K(\mathbf{r})=\left(1-\frac{V(\mathbf{r})}{2c^2}\right)^{-1}. \tag{7}$$

We can rewrite Eq. (6) as

$$H_{\text{ZORA}}=V(\mathbf{r})+\boldsymbol{\pi}\frac{K(\mathbf{r})}{2}\boldsymbol{\pi}+\frac{K^2(\mathbf{r})}{4c^2}\boldsymbol{\sigma}\cdot[\nabla V(\mathbf{r})\times\mathbf{p}] -\frac{1}{c}K(\mathbf{r})\boldsymbol{\sigma}\cdot\mathbf{B}. \tag{8}$$

The local function $K(\mathbf{r})$ determines the influence of relativity on the system. For a valence electron in a weak potential $K=1$, in which case Eq. (6) reduces to the nonrelativistic Levy–Leblond Hamiltonian.[13,14] Close to the nucleus $K<1$ and thus relativity has a direct influence on the electrons. To a good approximation a valence electron in this region will experience the strong Coulomb potential, screened by the core electrons, independent of the chemical environment. Consequently we may calculate $K(\mathbf{r})$ using the potential screened by the core electrons generated from an atomic calculation.

The final two terms in Eq. (8) represent spin–orbit coupling and the coupling between the spin and magnetic field, respectively. We neglect these two terms, the remaining terms in Eq. (8) form the basis of the scalar relativistic approximation. The effects of spin–orbit coupling can be considerable for heavy elements (e.g., Ref. 4) and is known to be significant for the shielding of light elements bonded to heavy atoms. However we shall examine only scalar relativistic effects.

In order to calculate magnetic response properties, such as NMR chemical shieldings, we require an expression for the induced orbital current density. We use the continuity equation,

$$\frac{\partial n_{\text{ZORA}}(\mathbf{r},t)}{\partial t}=\nabla\mathbf{J}_{\text{ZORA}}(\mathbf{r},t) \tag{9}$$

and note that within the zeroth-order approximation the charge density, $n_{\text{ZORA}}(\mathbf{r})$, is given by $n_{\text{ZORA}}(\mathbf{r})=\langle\Psi_{\text{ZORA}}|\Sigma_N\delta(\mathbf{r}-\mathbf{r}')|\Psi_{\text{ZORA}}\rangle$. The derivative with respect to time can be obtained by using the time-dependent form of the ZORA equation,

$$\frac{\partial|\Psi_{\text{ZORA}}\rangle}{\partial t}=H_{\text{ZORA}}|\Psi_{\text{ZORA}}\rangle. \tag{10}$$

The electric current operator, $\mathbf{J}_{\text{ZORA}}(\mathbf{r}')$, can thus be written as

$$\mathbf{J}_{\text{ZORA}}(\mathbf{r}')=K(\mathbf{r}')\left[\mathbf{J}^{p}(\mathbf{r}')-\frac{\mathbf{A}(\mathbf{r}')}{c}|\mathbf{r}'\rangle\langle\mathbf{r}'|\right], \tag{11}$$

where

$$\mathbf{J}^{p}(\mathbf{r}')=\frac{\mathbf{p}|\mathbf{r}'\rangle\langle\mathbf{r}'|+|\mathbf{r}'\rangle\langle\mathbf{r}'|\mathbf{p}}{2}. \tag{12}$$

C. Projector augmented wave

Van de Walle and Blöchl[15] have introduced a method in which all-electron properties can be extracted from a pseudopotential calculation. In their projector augmented wave (PAW) approach the all-electron wave function Ψ is derived from the pseudo-wave-function $\tilde{\Psi}$ by means of a linear transformation, $\mathcal{T}$,

$$|\Psi\rangle=\mathcal{T}|\tilde{\Psi}\rangle, \tag{13}$$

where

$$\mathcal{T}=\mathbf{1}+\sum_{\mathbf{R},n}[|\phi_{\mathbf{R},n}\rangle-|\tilde{\phi}_{\mathbf{R},n}\rangle]\langle\tilde{p}_{\mathbf{R},n}|, \tag{14}$$

$|\phi_{\mathbf{R}n}\rangle$, $|\tilde{\phi}_{\mathbf{R}n}\rangle$ are all-electron and pseudopartial waves and $\langle\tilde{p}_{\mathbf{R}n}|$ are a set of projectors such that $\langle\tilde{p}_{\mathbf{R}n}|\tilde{\phi}_{\mathbf{R}'m}\rangle$

$=\delta_{\mathbf{RR}'}\delta_{nm}$. Each projector and partial wave is an atomic-like function centered on an atomic site $\mathbf{R}$, and the index n refers to both the angular momentum quantum numbers and to an additional number which is used if there is more than one projector per angular momentum channel.

For each atom we define an augmentation region $\Omega_{\mathbf{R}}$. The following conditions are imposed: (i) outside $\Omega_{\mathbf{R}} |\phi_{\mathbf{R}n}\rangle$ and $|\tilde{\phi}_{\mathbf{R}n}\rangle$ coincide, (ii) outside $\Omega_{\mathbf{R}}$ the projectors $\langle\tilde{p}_{\mathbf{R}n}|$ vanish, (iii) within $\Omega_{\mathbf{R}}$ the $|\phi_{\mathbf{R}n}\rangle$ form a complete set for the valence wave functions, and (iv) the augmentation regions belonging to different atoms do not overlap.

Under these conditions, for an all-electron operator O, the corresponding pseudo-operator, $\tilde{O}$, is given by

$$\tilde{O}=O+\sum_{\mathbf{R},n,m}|\tilde{p}_{\mathbf{R},n}\rangle[\langle\phi_{\mathbf{R},n}|O|\phi_{\mathbf{R},m}\rangle-\langle\tilde{\phi}_{\mathbf{R},n}|O|\tilde{\phi}_{\mathbf{R},m}\rangle]\times\langle\tilde{p}_{\mathbf{R},m}|. \qquad (15)$$

We may use Eq. (15) to calculate all-electron observables from pseudopotential calculations (e.g., hyperfine parameters,[15] electric field gradients,[16] core level spectroscopy).[17] However, for magnetic response properties Eq. (14) is not sufficient. In a uniform magnetic field a rigid translation of all the atoms in the system by a vector $\mathbf{t}$ causes the wave functions to pick up an additional field-dependent phase factor,

$$\langle\mathbf{r}|\Psi_n'\rangle=e^{(i/2c)\mathbf{r}\cdot\mathbf{t}\times\mathbf{B}}\langle\mathbf{r}-\mathbf{t}|\Psi_n\rangle. \qquad (16)$$

The wave functions reconstructed using the PAW operator of Eq. (14) do not transform according to Eq. (16). In order to preserve translational invariance in a magnetic field the PAW method was generalized in Ref. 10 leading to the GIPAW approach. Within GIPAW the field-dependent transform operator, $\mathcal{T}_{\mathbf{B}}$, is

$$\mathcal{T}_{\mathbf{B}}=1+\sum_{\mathbf{R},n}e^{(i/2c)\mathbf{r}\cdot\mathbf{R}\times\mathbf{B}}[|\phi_{\mathbf{R},n}\rangle-|\tilde{\phi}_{\mathbf{R},n}]\langle\tilde{p}_{\mathbf{R},n}|e^{-(i/2c)\mathbf{r}\cdot\mathbf{R}\times\mathbf{B}} \qquad (17)$$

In the following, we indicate with a bar the pseudo-wave-functions and operators obtained using the $\mathcal{T}_{\mathbf{B}}$ operator by analogy to Blöchl's use of the tilde. The GIPAW pseudo-operator $\overline{O}=\mathcal{T}_{\mathbf{B}}^{+}O\mathcal{T}_{\mathbf{B}}$ corresponding to a local or a semilocal operator O is given by

$$\begin{aligned}\overline{O}=O+\sum_{\mathbf{R},n,m}&e^{(i/2c)\mathbf{r}\cdot\mathbf{R}\times\mathbf{B}}|\tilde{p}_{\mathbf{R},n}\rangle\\&\times[\langle\phi_{\mathbf{R},n}|e^{-(i/2c)\mathbf{r}\cdot\mathbf{R}\times\mathbf{B}}Oe^{(i/2c)\mathbf{r}\cdot\mathbf{R}\times\mathbf{B}}|\phi_{\mathbf{R},m}\rangle\\&-\langle\tilde{\phi}_{\mathbf{R},i}|e^{-(i/2c)\mathbf{r}\cdot\mathbf{R}\times\mathbf{B}}Oe^{(i/2c)\mathbf{r}\cdot\mathbf{R}\times\mathbf{B}}|\tilde{\phi}_{\mathbf{R},m}\rangle]\\&\times\langle\tilde{p}_{\mathbf{R},m}|e^{-(i/2c)\mathbf{r}\cdot\mathbf{R}\times\mathbf{B}}.\end{aligned} \qquad (18)$$

D. NMR chemical shielding

The chemical shielding tensor $\overleftrightarrow{\sigma}(\mathbf{r})$ is defined as the ratio between a uniform external magnetic field, $\mathbf{B}$, and the induced magnetic field, $\mathbf{B}_{\text{in}}^{(1)}(\mathbf{r})$,

$$\mathbf{B}_{\text{in}}^{(1)}(\mathbf{r})=-\overleftrightarrow{\sigma}(\mathbf{r})\mathbf{B}=\frac{1}{c}\int d^3r'\,\mathbf{j}^{(1)}(\mathbf{r}')\times\frac{\mathbf{r}-\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|^3}, \qquad (19)$$

where $\mathbf{j}^{(1)}$ is the first-order induced electric current.

Following the procedure outlined in Ref. 10, to calculate the shielding tensor we must derive relativistic forms of the magnetic pseudo-Hamiltonian and the pseudocurrent operator. The scalar relativistic ZORA Hamiltonian is

$$H_{\text{ZORA}}=V(\mathbf{r})+\boldsymbol{\pi}\frac{K}{2}\boldsymbol{\pi}. \qquad (20)$$

In the presence of a uniform magnetic field, $\mathbf{B}$, and choosing the symmetric gauge, $\mathbf{A}(\mathbf{r})=\frac{1}{2}\mathbf{B}\times\mathbf{r}$, we can expand Eq. (20) in powers of $\mathbf{B}$,

$$H_{\text{ZORA}}=V(\mathbf{r})+\mathbf{p}\frac{K}{2}\mathbf{p}+\frac{K}{4c}\mathbf{B}\cdot\mathbf{L}+\mathbf{B}\cdot\mathbf{L}\frac{K}{4c}+\mathcal{O}(\mathbf{B}^2). \quad (21)$$

Applying the GIPAW transformation to Eq. (21) we find that the ZORA pseudo Hamiltonian is identical in form to the nonrelativistic pseudo-Hamiltonian (see the Appendix). Relativistic effects are confined to the nonlocal part of the pseudopotential, $V_{\mathbf{R}}^{\text{nl}}$, which is generated from a relativistic atomic calculation.

To first order in $\mathbf{B}$ the pseudo-Hamiltonian can be written

$$\overline{H}_{\text{ZORA}}=\frac{1}{2}\mathbf{p}^2+V^{\text{loc}}(\mathbf{r})+\sum_{\mathbf{R}}V_{\mathbf{R}}^{\text{nl}}+\frac{1}{2c}\left(\mathbf{L}+\sum_{\mathbf{R}}\mathbf{R}\times\mathbf{v}_{\mathbf{R}}^{\text{nl}}\right)\cdot\mathbf{B}, \qquad (22)$$

where

$$\mathbf{v}_{\mathbf{R}}^{\text{nl}}=\frac{1}{i}[\mathbf{r},V_{\mathbf{R}}^{\text{nl}}]. \qquad (23)$$

By a similar approach we obtain the GIPAW current operator from Eq. (11);

$$\begin{aligned}\overline{\mathbf{J}}(\mathbf{r}')=\mathbf{J}^p(\mathbf{r}')-\frac{\mathbf{B}\times\mathbf{r}'}{2c}|\mathbf{r}'\rangle\langle\mathbf{r}'|+\sum_{\mathbf{R}}&e^{(i/2c)\mathbf{r}\cdot\mathbf{R}\times\mathbf{B}}\\&\times[\Delta\mathbf{J}_{\mathbf{R}}^{\text{p}}(\mathbf{r}')+\Delta\mathbf{J}_{\mathbf{R}}^{\text{d}}(\mathbf{r}')]e^{-(i/2c)\mathbf{r}\cdot\mathbf{R}\times\mathbf{B}},\end{aligned} \qquad (24)$$

where

$$\begin{aligned}\Delta\mathbf{J}_{\mathbf{R}}^{p}(\mathbf{r}')=\sum_{n,m}&|\tilde{p}_{\mathbf{R},n}\rangle[\langle\phi_{\mathbf{R},n}|K(\mathbf{r}')\mathbf{J}^p(\mathbf{r}')|\phi_{\mathbf{R},m}\rangle\\&-\langle\tilde{\phi}_{\mathbf{R},n}|\mathbf{J}^p(\mathbf{r}')|\tilde{\phi}_{\mathbf{R},m}\rangle]\langle\tilde{p}_{\mathbf{R},m}|\end{aligned} \qquad (25)$$

is the paramagnetic augmentation operator, and

$$\begin{aligned}\boldsymbol{\Delta}\mathbf{J}_{\mathbf{R}}^{d}(\mathbf{r}')=-\frac{\mathbf{B}\times(\mathbf{r}'-\mathbf{R})}{2c}\sum_{n,m}&|\tilde{p}_{\mathbf{R},n}\rangle[\langle\phi_{\mathbf{R},n}|\mathbf{r}'\rangle K(\mathbf{r}')\\&\times\langle\mathbf{r}'|\phi_{\mathbf{R},m}\rangle-\langle\tilde{\phi}_{\mathbf{R},n}|\mathbf{r}'\rangle\langle\mathbf{r}'|\tilde{\phi}_{\mathbf{R},m}\rangle]\langle\tilde{p}_{\mathbf{R},m}|\end{aligned} \qquad (26)$$

is the diamagnetic augmentation operator.

In the nonrelativistic limit, $K=1$ and we recover the form of the GIPAW current operator obtained in Ref. 10. Note that in Eqs. (25) and (26) the relativistic parameter K is contained only within the atomic all-electron matrix elements.

Pickard and Mauri[10] use density functional perturbation theory to derive an expression for the induced current in both finite and infinitely periodic systems. Following the same procedure we obtain identical expressions using the modified GIPAW augmentation operators, Eqs. (25) and (26).

The total valence current is given by the current due to the pseudized valence electrons plus the diamagnetic and paramagnetic augmentation currents. We could combine these three contributions and apply the Biot–Savart law to find the total valence shielding. Instead we follow Ref. 10 and take advantage of the linearity of the Biot–Savart law to solve for each of the three current contributions giving; σ_{bare}, the shielding from the response of the pseudized valence electrons, $\sigma_{\Delta d}$ the shielding from the diamagnetic GIPAW current augmentation, and $\sigma_{\Delta p}$ the shielding from the paramagnetic GIPAW current augmentation. When added to the contribution due to the core electrons, σ_{core}, calculated separately in an atomic code, we obtain the total chemical shielding. The core and bare contributions are unaffected by using the ZORA current. However, both the diamagnetic and paramagnetic augmentation terms are modified from their nonrelativistic forms by the inclusion of the factor of K.

E. Discussion

For the pseudocurrent operator, Eq. (24), as for the pseudomagnetic Hamiltonian, Eq. (22), we find the effects of relativity (through the inclusion of K) are contained purely within the GIPAW augmentation terms. This is due to the fact that the region in which $K \neq 1$, where the electrons can be considered to be relativistic, is localized close to the nucleus. For the current operator the augmentation terms are given by Eqs. (26) and (25). For the pseudo-Hamiltonian the augmentation term is just the nonlocal part of the pseudopotential.

As relativistic effects are confined to the GIPAW augmentation terms, the majority of any computational implementation of this approach (e.g., the calculation of the ground state charge density, the perturbed and unperturbed wave functions, and so on) need not be altered from a nonrelativistic implementation. Only the calculation of the GIPAW augmentation terms differ through the inclusion of the local function $K(\mathbf{r})$, which requires only a single matrix overlap. These augmentation terms depend only on the atomic species and need only be calculated once. Consequently, there is essentially no extra computational cost associated with the inclusion of relativistic effects within the ZORA/GIPAW approximation.

III. CHEMICAL SHIELDING OF Se AND Te COMPOUNDS

The methods described in Sec. II were used to examine the chemical shielding in a range of selenium and tellurium containing compounds. These elements were chosen as Se and Te have been the focus of previous first principles density functional studies allowing us to compare our pseudopotential results with all-electron calculations.

A. Implementation

The method described in Sec. II D has been implemented in a parallelized plane-wave pseudopotential electronic structure code. The chemical shielding tensors were converged to within 1 ppm using a plane-wave cut-off of 80 Ry, large supercells, and a 2×2×2 Monkhorst–Pack k-point grid. All calculations used the Perdew–Burke–Ernzerhof[18] exchange-correlation functional. The chemical shielding tensors due to the core electrons where calculated using the Lamb formula[19] and it relativistic equivalent[20] (neglecting spin dependent terms). The results are given in Table I. Numerous schemes exist to treat single atom calculations relativistically with minor computational cost. To be consistent with our scalar relativistic approximation we use the j-averaged form of the radial relativistic Kohn–Sham equations.[21] This includes the effects of spin–orbit coupling on the orbital motion of the electrons but neglects any shielding effects of the induced spin density. In principle we could use a ZORA-based atomic code.

TABLE I. Values of core shieldings for Se and Te from relativistic and nonrelativistic calculations.

Atom	Core	δ_{core} Nonrelativistic	δ_{core} Relativistic
Se	$1s\ 2s\ 2p\ 3s\ 3p\ 3d$	2932.12	2992.31
Te	$1s\ 2s\ 2p\ 3s\ 3p\ 4s\ 3d\ 4p\ 4d$	5307.39	5568.31

The pseudopotentials used were of the Troullier–Martins form.[22] For Se only the $4s$ and $4p$ states were treated as valence, states below these in energy were included in the core. A pseudization core radius of 1.9 bohr was used. For Te the core contained all states except $5s$ and $5p$, which were treated as valence. The pseudization core radius was 2.2 bohr. For both elements, the GIPAW augmentation used two projectors in each of the s, p, and d channels. For the first row elements the $1s$ states were treated as core states. The cutoff radii for C and F were 1.6 and 1.3 bohr, respectively, and the pseudization core radius for H was 1.2 bohr.

B. Results

NMR chemical shieldings were calculated for a range of Selenium and Tellurium compounds chosen to span the chemical shift range for each element. For all molecules the geometries were optimized using relativistic pseudopotentials.[23] No symmetry constraints were applied to obtain a realistic estimate of the level of accuracy obtainable for large, low-symmetry structures.

Nonrelativistic calculations were performed with pseudopotentials generated from a nonrelativistic atomic code and used GIPAW augmentation operators in their nonrelativistic ($K=1$) form. Relativistic calculations used pseudopotentials generated from a relativistic atomic code. The relativistic GIPAW operators derived in Sec. II D were used. In order to examine the effect of the relativistic GIPAW augmentation operators, mixed calculations were also performed using relativistic pseudopotentials and nonrelativistic GIPAW operators.

The most stringent test of calculated shieldings is the comparison with experimental absolute shieldings. When comparing relative shifts a large proportion of the effects due to relativity cancel. Absolute shielding scales exist for most

TABLE II. ^{77}Se chemical shieldings. Comparison of methods.

	δ_{tot} nonrelativistic		δ_{tot} relativistic	
Molecule	GIPAW	SR-MZ[a]	GIPAW	Experiment[b]
SeH_2	2138.6		2198.1	2162
$Se(CH_3)_2$[c]	1734.5	1668	1803.2	1830
SeF_6	1003.7	953	1079.8	1199
SeF_4	544.7	494	624.1	747
$SeHCH_3$	1911.3	1837	1975.3	1985
Mean absolute error[d]	118		63	

[a] Reference 24.

[b] Revised experimental results (see the text) collected in Ref. 24.

[c] Staggered–staggered conformation.

[d] Relative to revised experimental results.

TABLE IV. ^{125}Te chemical shieldings. Comparison of methods.

	δ_{tot} nonrelativistic		δ_{tot} relativistic		
Molecule	GIPAW	R-MSZ[a]	GIPAW	R-MSZ[a]	Experiment[b]
TeH_2	3591.3		3833.9	3761.4	4009
$Te(CH_3)_2$[c]	2779.9	2868.2	3053.10	3050.3	3388
$Te(CH_3)_4$	3026.6	3018.6	3263.0	3189.2	3455
TeF_6	2180.6	2260.0	2416.8	2448.1	2845±130
$(TeCF_2)_2$[d]	600.1	528.0	890.06	614.3	1066
$(TeCF_2)_2$[d]	665.5		957.59		
Mean absolute error[e]	511		198		

[a] Reference 25.

[b] Revised experimental results as Ref. 25.

[c] Staggered–staggered conformation.

[d] As we use nonsymmetrized geometries slightly different values are obtained for the two Te atoms.

[e] Relative to revised experimental results.

light nuclei, however they have been determined for only a few heavy nuclei. Experimental shielding scales for Se and Te have been determined by Jameson and Jameson.[26] However their analysis explicitly neglects any contribution to the chemical shielding from a spin-density induced by spin–orbit coupling. It is therefore to be expected that calculations performed within the scalar relativistic approximation should be in reasonable agreement with shieldings on this shielding scale. However one cannot deduce anything about the importance of spin–orbit coupling by such agreement.

In a recent paper[27] it was claimed that the effects of spin–orbit coupling on Te absolute shieldings is large (approximately 1700 ppm). It is clear that more work on the effects of spin–orbit coupling on the shifts of fourth and fifth row elements is necessary, in particular to define reliable absolute shielding scales for Se and Te. Work on extending our pseudopotential method to include spin–orbit effects is in progress.

Although we suggest that the only true comparison to experiment is provided by relative shifts, absolute shieldings provide a good comparison to other first principles calculations. Calculated absolute shieldings are summarized in Tables II and IV. Where available, first principles density functional results from Ref. 24 for Se and Ref. 25 for Te are given.

The first principles DFT results of Refs. 24 and 25 are based on Slater-type atomic orbitals and use a frozen core approximation. It should be noted that the frozen cores employed in these calculations are smaller than the cores used in our pseudopotential calculations. For example, in Ref. 24 the $3s$, $3p$ and $3d$ levels of Se and in Ref. 25 the $4d$ levels of Te are included in the valence levels. In our pseudopotential treatment all these states are included in the core. The relativistic approximation employed for Te in Ref. 25 is based on the scalar relativistic Pauli approximation to the Dirac equation. A mixture of experimental and optimized geometries were used in Refs. 24 and 25.

In Tables II and IV we also present experimental results on the scalar-relativistic absolute scales of Ref. 26. These scales are based on an estimate of the relativistic correction to the diamagnetic free atom shieldings. In Ref. 25 the estimate for Te is discussed and it is shown by a ‘‘fully-relativistic Dirac DFT’’ calculation on the free Te atom that it is a severe overestimate. In Ref. 25 a scale reduced by 900 ppm is proposed. We concur with this result, and propose that a similar reduction is necessary for selenium. We calculate the difference between the relativistic and nonrelativistic free atom shielding to be 61 ppm compared to the estimate of 300 ppm of Ref. 26. Accordingly we propose a revised shielding scale reduced by 239 ppm.

As can be seen in Table II, for selenium the agreement between our nonrelativistic calculations and Ref. 24 is good. We find that the inclusion of relativistic effects typically increases the ^{77}Se absolute shielding by 60–70 ppm. The mean absolute deviation from the revised experimental shieldings is 118 ppm in the nonrelativistic case. Relativistic calculations reduce this deviation to 63 ppm. Most of the difference between relativistic and nonrelativistic calculations cancels when comparing the chemical shifts relative to $Se(CH_3)_2$,

TABLE III. Experimental and calculated ^{77}Se chemical shifts for a range of compounds.

	Nonrelativistic	Relativistic	Experiment[a]
$Se(CH_3)_2$[b]	(0.0)	(0.0)	(0.0)
SeH_2	−404.1	−394.9	−345(g)
SeF_6	730.8	723.5	631(g)
SeF_4	1189.8	1174.0	1083
$SeHCH_3$	−176.8	−172.1	−155(g)

[a] Experimental results collected in Ref. 24.

[b] Staggered–staggered conformation.

TABLE V. Experimental and calculated ^{125}Te chemical shifts for a range of compounds.

	Nonrelativistic	Relativistic	Experiment[a]
$Te(CH_3)_2$[b]	(0.0)	(0.0)	(0.0)
TeH_2	−811.4	−780.8	−621
$Te(CH_3)_4$	−246.8	−209.9	−67
TeF_6	599.3	636.3	543±130
$(TeCF_2)_2$[c]	2179.8	2163.0	2321
$(TeCF_2)_2$[c]	2114.4	2095.5	

[a] Experimental results collected in Ref. 25.

[b] Staggered–staggered conformation.

[c] As we use nonsymmetrized geometries slightly different values are obtained for the two Te atoms.

TABLE VI. Selenium shieldings: Effects of relativistic GIPAW operators.

Molecule	ZORA GIPAW operators[a] δ_{bare}	δ_{dia}	δ_{para}	δ_{total}	Nonrelativistic GIPAW operators[b] δ_{bare}	δ_{dia}	δ_{para}	δ_{total}
SeH_2	45.71	8.02	−847.92	2198.11	45.71	8.25	−890.35	2155.90
$Se(CH_3)_2$	33.25	8.00	−1230.33	1803.22	33.25	8.23	−1291.61	1794.64
SeF_6	−0.37	8.40	−1920.57	1079.76	−0.37	8.59	−2005.91	994.62
SeF_4	−8.53	7.78	−2367.44	624.12	−8.53	8.00	−2480.92	510.86
$SeHCH_3$	38.50	8.01	−1063.53	1975.29	38.50	8.23	−1116.62	1922.42

[a] Using relativistic pseudopotentials and the relativistic GIPAW current operators of this work.
[b] Using relativistic pseudopotentials and the nonrelativistic GIPAW current operators of Ref. 10.

the standard for Se (see Table III). In this case the maximum change in the chemical shift on including relativity is just 9 ppm, which occurs for SeH_2.

As expected, the effects of relativity on the Te shieldings are much greater than for Se. Relativistic effects increase the absolute shieldings by 200–300 ppm and decrease the mean absolute deviation from the revised experimental shieldings from 511 to 198 ppm (see Table IV). Again most of this difference cancels out if we compare the chemical shifts relative to the Te standard, which is $Te(CH_3)_2$. Here the maximum change is 37 ppm for TeF_6. The nonrelativistic Te shieldings are in close agreement with Ref. 25 (Table V). The relativistic shieldings are also in broadly good agreement but we note that our results are consistently closer to the experimental values. This is most likely due to a combination of a more complete basis set, and the fact that the ZORA method provides a better description of valence electrons than the Pauli approximation.[5] However, a detailed comparison of these methods is beyond the scope of the present work.

In Tables VI and VII we compare calculations performed with relativistic pseudopotentials and both relativistic and nonrelativistic GIPAW current operators, so as to assess the importance of the ZORA-GIPAW correction. We also break down the contributions to the total chemical shieldings of the valence electrons. The bare term, δ_{bare}, will be identical in each case. From Tables VI and VII it can be seen that the diamagnetic contribution is only slightly smaller using relativistic operators, but the paramagnetic term is reduced significantly. Combining the GIPAW augmentation operators with the Biot–Savart law to calculate the induced magnetic field we find that the matrix elements of the diamagnetic term are proportional to $1/r$, whilst those of the paramagnetic term are proportional to $1/r^3$. The $1/r^3$ character of δ_{para} weights the matrix elements strongly into the region close to the nucleus, where the factor of K damps their contribution.

It is clear that the influence of relativity on the valence electrons in the core region is a significant factor in the NMR chemical shielding and it cannot be accounted for using relativistic pseudopotentials alone.

Finally we note that from Tables VI and VII it is clear that the dominant contribution to the chemical shifts in Se and Te comes from the paramagnetic augmentation. Pseudopotential methods such as Refs. 28 and 29, which do not take account of the pseudization of the valence wave functions, cannot correctly describe the chemical shifts of nuclei heavier than Ne.

IV. CONCLUSIONS

We have presented a method for the efficient calculation of NMR shielding tensors for heavy elements. Computational efficiency is obtained by using pseudopotentials to reduce the number of electronic degrees of freedom. Relativity is introduced by means of the scalar relativistic ZORA approach to the Dirac equation. Using this method a scalar relativistic calculation on TeH_2 has roughly the same computational cost as a nonrelativistic calculation on OH_2 in contrast to a traditional all-electron approach. This opens up the possibility of calculating the chemical shielding of heavy atom nuclei in molecular and periodic systems containing several hundred atoms, e.g., calculations of ^{129}Xe shieldings in zeolites.

TABLE VII. Tellurium shieldings: Effect of relativistic GIPAW operators.

Molecule	ZORA GIPAW operators[a] δ_{bare}	δ_{dia}	δ_{para}	δ_{total}	Nonrelativistic GIPAW operators[b] δ_{bare}	δ_{dia}	δ_{para}	δ_{total}
TeH_2	36.32	7.04	−1777.77	3833.90	36.32	7.32	−1988.02	3623.92
$Te(CH_3)_2$	26.00	7.00	−2548.20	3053.10	26.00	7.27	−2849.26	2752.32
$Te(CH_3)_4$	14.98	7.09	−2327.39	3262.98	14.98	7.36	−2567.05	3023.60
TeF_6	2.71	7.39	−3161.61	2416.80	2.71	7.63	−3485.15	2093.48
$(TeCF_2)_2$	3.09	6.95	−4688.30	890.06	3.09	7.23	−5256.09	322.55
$(TeCF_2)_2$	3.70	6.98	−4621.40	957.59	3.70	7.26	−5180.78	398.49

[a] Using relativistic pseudopotentials and the relativistic GIPAW current operators of this work.
[b] Using relativistic pseudopotentials and the nonrelativistic GIPAW current operators of Ref. 10.

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APPENDIX: ZORA PSEUDO-HAMILTONIAN

The all-electron ZORA Hamiltonian can be written, in its scalar-relativistic form, as

$$H_{\mathrm{ZORA}}=V(\mathbf{r})+\boldsymbol{\pi}\frac{K(\mathbf{r})}{2}\boldsymbol{\pi}. \tag{A1}$$

Using Eq. (18) the corresponding GIPAW pseudo-operator is

$$\begin{aligned}\bar{H}_{\mathrm{ZORA}}=&\,V(\mathbf{r})+\boldsymbol{\pi}\frac{K(\mathbf{r})}{2}\boldsymbol{\pi}+\sum_{\mathbf{R},n,m}e^{\theta}|\tilde{p}_{\mathbf{R},n}\rangle\\&\times\left[\left\langle\phi_{\mathbf{R},n}\left|e^{-\theta}\left(\boldsymbol{\pi}\frac{K(\mathbf{r})}{2}\boldsymbol{\pi}+V(\mathbf{r})\right)e^{\theta}\right|\phi_{\mathbf{R},m}\right\rangle\right.\\&\left.-\left\langle\tilde{\phi}_{\mathbf{R},i}\left|e^{-\theta}\left(\boldsymbol{\pi}\frac{K(\mathbf{r})}{2}\boldsymbol{\pi}V(\mathbf{r})\right)e^{\theta}\right|\tilde{\phi}_{\mathbf{R},m}\right\rangle\right]\\&\times\langle\tilde{p}_{\mathbf{R},m}|e^{-\theta},\end{aligned} \tag{A2}$$

where $\theta=(i/2c)\mathbf{r}\cdot\mathbf{R}\times\mathbf{B}$.

This can be written as

$$\begin{aligned}\bar{H}_{\mathrm{ZORA}}=&\,V^{\mathrm{loc}}(\mathbf{r})+\frac{1}{2}\boldsymbol{\pi}\cdot\boldsymbol{\pi}+(V(\mathbf{r})-V^{\mathrm{loc}}(\mathbf{r}))\\&+\boldsymbol{\pi}\frac{(K(\mathbf{r})-1)}{2}\boldsymbol{\pi}+\sum_{\mathbf{R},n,m}e^{\theta}|\tilde{p}_{\mathbf{R},n}\rangle\\&\times\left[\left\langle\phi_{\mathbf{R},n}\left|e^{-\theta}\left(\boldsymbol{\pi}\frac{K(\mathbf{r})}{2}\boldsymbol{\pi}+V(\mathbf{r})\right)e^{\theta}\right|\phi_{\mathbf{R},m}\right\rangle\right.\\&\left.-\left\langle\tilde{\phi}_{\mathbf{R},i}\left|e^{-\theta}\left(\boldsymbol{\pi}\frac{K(\mathbf{r})}{2}\boldsymbol{\pi}+V(\mathbf{r})\right)e^{\theta}\right|\tilde{\phi}_{\mathbf{R},m}\right\rangle\right]\\&\times\langle\tilde{p}_{\mathbf{R},m}|e^{-\theta},\end{aligned} \tag{A3}$$

where $V^{\mathrm{loc}}(\mathbf{r})$ is a purely local function chosen such that $V(\mathbf{r})-V^{\mathrm{loc}}(\mathbf{r})$ is localized within the augmentation region, $\Omega_{\mathbf{R}}$. As K only differs from 1 near to the nucleus, the operator

$$\boldsymbol{\pi}\frac{(K(\mathbf{r})-1)}{2}\boldsymbol{\pi}$$

also acts only within $\Omega_{\mathbf{R}}$. Using this localization and the fact that the projectors and the pseudopartial waves form a complete set, we write Eq. (A3) as

$$\begin{aligned}\bar{H}_{\mathrm{ZORA}}=&\,V^{\mathrm{loc}}(\mathbf{r})+\frac{1}{2}\boldsymbol{\pi}\cdot\boldsymbol{\pi}+\sum_{\mathbf{R},n,m}e^{\theta}|\tilde{p}_{\mathbf{R},n}\rangle\\&\times\left[\left\langle\phi_{\mathbf{R},n}\left|e^{-\theta}\left(\boldsymbol{\pi}\frac{K(\mathbf{r})}{2}\boldsymbol{\pi}+V(\mathbf{r})\right)e^{\theta}\right|\phi_{\mathbf{R},m}\right\rangle\right.\\&\left.-\langle\tilde{\phi}_{\mathbf{R},i}|e^{-\theta}(\boldsymbol{\pi}\cdot\boldsymbol{\pi}+V^{\mathrm{loc}}(\mathbf{r}))e^{\theta}|\tilde{\phi}_{\mathbf{R},m}\rangle\right]\\&\times\langle\tilde{p}_{\mathbf{R},m}|e^{-\theta}.\end{aligned} \tag{A4}$$

Using the identity

$$\begin{aligned}&e^{-(i/2c)\mathbf{r}\cdot\mathbf{R}\times\mathbf{B}}\left(\mathbf{p}+\frac{1}{c}\mathbf{A}(\mathbf{r})\right)G(\mathbf{r})\left(\mathbf{p}+\frac{1}{c}\mathbf{A}(\mathbf{r})\right)e^{(i/2c)\mathbf{r}\cdot\mathbf{R}\times\mathbf{B}}\\&=\left(\mathbf{p}+\frac{1}{c}\mathbf{A}(\mathbf{r}-\mathbf{R})\right)G(\mathbf{r})\left(\mathbf{p}+\frac{1}{c}\mathbf{A}(\mathbf{r}-\mathbf{R})\right),\end{aligned} \tag{A5}$$

where $G(\mathbf{r})$ is a local function, we obtain

$$\begin{aligned}\bar{H}_{\mathrm{ZORA}}=&\,V^{\mathrm{loc}}(\mathbf{r})+\frac{1}{2}\boldsymbol{\pi}\cdot\boldsymbol{\pi}+\sum_{\mathbf{R},n,m}e^{\theta}|\tilde{p}_{\mathbf{R},n}\rangle\\&\times\left[\left\langle\phi_{\mathbf{R},n}\left|\left(\boldsymbol{\pi}_{\mathbf{R}}\frac{K(\mathbf{r})}{2}\boldsymbol{\pi}_{\mathbf{R}}+V(\mathbf{r})\right)\right|\phi_{\mathbf{R},m}\right\rangle\right.\\&\left.-\langle\tilde{\phi}_{\mathbf{R},i}|(\boldsymbol{\pi}_{\mathbf{R}}\cdot\boldsymbol{\pi}_{\mathbf{R}}+V^{\mathrm{loc}}(\mathbf{r}))|\tilde{\phi}_{\mathbf{R},m}\rangle\right]\\&\times\langle\tilde{p}_{\mathbf{R},m}|e^{-\theta},\end{aligned} \tag{A6}$$

where $\boldsymbol{\pi}_{\mathbf{R}}=\mathbf{p}+(1/c)\mathbf{A}(\mathbf{r}-\mathbf{R})$.

We expand H in powers of B,

$$\bar{H}=\bar{H}^{(0)}+\bar{H}^{(1)}+O(B^2) \tag{A7}$$

and finally obtain

$$\bar{H}^{(0)}=\frac{1}{2}\mathbf{p}^2+V^{\mathrm{loc}}(\mathbf{r})+\sum_{\mathbf{R}}V_{\mathbf{R}}^{\mathrm{nl}}, \tag{A8}$$

where the nonlocal part of the pseudopotential, V^{nl}, is given by

$$V_{\mathbf{R}}^{\mathrm{nl}}=\sum_{n,m}|\tilde{p}_{\mathbf{R},n}\rangle a_{n,m}^{\mathbf{R}}\langle\tilde{p}_{\mathbf{R},m}|. \tag{A9}$$

The coefficients $a_{n,m}^{\mathbf{R}}$ are given by

$$\begin{aligned}a_{n,m}^{\mathbf{R}}=&\,\langle\phi_{\mathbf{R},n}|\left(\mathbf{p}\frac{K(\mathbf{r})}{2}\mathbf{p}+V(\mathbf{r})\right)|\phi_{\mathbf{R},m}\rangle\\&-\langle\tilde{\phi}_{\mathbf{R},i}|(\mathbf{p}^2+V^{\mathrm{loc}}(\mathbf{r}))|\tilde{\phi}_{\mathbf{R},m}\rangle.\end{aligned} \tag{A10}$$

The contribution to $\bar{H}$ linear in $\mathbf{B}$ is

$$\bar{H}^{(1)}=\frac{1}{2c}\left(\mathbf{L}+\sum_{\mathbf{R}}\mathbf{R}\times\mathbf{v}_{\mathbf{R}}^{\mathrm{nl}}\right)\cdot\mathbf{B}+\sum_{n,m}|\tilde{p}_{\mathbf{0},n}\rangle b_{n,m}^{(1)}\langle\tilde{p}_{\mathbf{0},m}|, \tag{A11}$$

where

$$\mathbf{v}_{\mathbf{R}}^{\mathrm{nl}}=\frac{1}{i}[\mathbf{r},V_{\mathbf{R}}^{\mathrm{nl}}], \tag{A12}$$

and

$$b_{n,m}^{(1)}=\frac{1}{2c}\mathbf{B}\cdot[\langle\phi_{\mathbf{0},n}|K\mathbf{L}|\phi_{\mathbf{0},m}\rangle-\langle\tilde{\phi}_{\mathbf{0},n}|\mathbf{L}|\tilde{\phi}_{\mathbf{0},m}\rangle]. \tag{A13}$$

For norm-conserving pseudopotentials $|\phi_m\rangle$ and $|\tilde{\phi}_m\rangle$ are eigenstates of L and L_z with the same norm within the augmentation region. The matrix elements $\langle\phi_{\mathbf{0},n}|\mathbf{L}|\phi_{\mathbf{0},m}\rangle$ are weighted outside of the nuclear region, into the region where $K=1$. As a result $b_{n,m}$ may be neglected and $\overline{H}^{(1)}$ is identical to the nonrelativistic form.[10]

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