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Qiming Sun, Wenjian Liu, Yunlong Xiao, et al.

Exact two-component relativistic theory for nuclear magnetic resonance parameters

Qiming Sun, Wenjian Liu,[a] Yunlong Xiao, and Lan Cheng
Beijing National Laboratory for Molecular Sciences, Institute of Theoretical and Computational Chemistry, State Key Laboratory of Rare Earth Materials Chemistry and Applications, College of Chemistry and Molecular Engineering, and Center for Computational Science and Engineering, Peking University, Beijing 100871, People's Republic of China

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An exact two-component (X2C) relativistic theory for nuclear magnetic resonance parameters is obtained by first a single block-diagonalization of the matrix representation of the Dirac operator in a magnetic-field-dependent basis and then a magnetic perturbation expansion of the resultant two-component Hamiltonian and transformation matrices. Such a matrix formulation is not only simple but also general in the sense that the various ways of incorporating the field dependence can be treated in a unified manner. The X2C dia- and paramagnetic terms agree individually with the corresponding four-component ones up to machine accuracy for any basis. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3216471]

I. INTRODUCTION

What is really measured in nuclear magnetic resonance (NMR) spectroscopy is the local effective magnetic field at the position of a resonant nucleus, which is intimately related to the electronic structure in the vicinity of the nucleus. As such, NMR parameters such as nuclear magnetic shielding (NMS) and indirect spin-spin coupling (SSC) tensors are intrinsically all-electron relativistic properties. Various quasirelativistic methods have been developed in the past, including first order perturbation approaches,[1,2] zeroth order regular approximation,[3–5] Douglas–Kroll–Hess type approximation,[6–12] and second order regular approximation[13–15] to the normalized elimination of the small component (NESC).[16] While such approximate methods are very useful for elucidating the various physical contributions and meanwhile work well for chemical shifts, they cannot provide accurate absolute NMS and SSC scales for heavy elements, as the inherent approximations therein arise solely from the atomic cores, precisely the regions sampled by the parameters. An exact treatment of the relativistic effects demands in principle a four-component theory based on the Dirac operator. Satisfactory formulations[17–22] of such a theory appear only rather recently, which demonstrate that the diamagnetism that is "missed" in the traditional formulation can be captured in a natural way. A direct consequence is that the contributions of "nightmare" negative energy states are reduced to order c^{-2} such that standard energy-optimized basis sets are already sufficient for reliable absolute NMS scales.[19] The power of such new formulations will soon be witnessed. On the other hand, an exact two-component (X2C) treatment of the relativistic effects should also be possible. The first attempt along this direction was made by Ootani *et al.*[23] who extended the infinite order two-component scheme of Barysz and Sadlej[24] to the calculation of NMS. Such an *operator* formulation invokes four steps. That is, the vector-potential-independent part of the Dirac operator is first decoupled exactly in two steps.[24] The two unitary transformations are directly used to transform the vector potential part of the Dirac operator, and the result is then decoupled to first order with respect to the vector potential via an additional exponential-type unitary operator. The final step is the magnetic perturbation expansion of the so-obtained two-component (analytical) Hamiltonian. As the electronic energy is correct to third order in the magnetic perturbation, the formalism is exact for NMS. However, the formalism has several drawbacks. (1) While a diamagnetic term is obtained naturally, its evaluation involves both the positive and negative energy states of the unperturbed Hamiltonian, which leaves the formalism essentially out of the realm of two-component theories. (2) The magnetic decoupling involves also the vector potential due to the nuclear magnetic point dipole moment so as to result in severe singularities or numerical instabilities.[18] (3) The particular transformations render the corrections for two-electron picture change errors very difficult. Here we show that all such problems can be avoided by going to a *matrix* formulation. That is, the matrix representation of the full Dirac operator in a magnetic-field-dependent basis can be block-diagonalized in a single step, just like the previous matrix formulation of the X2C (algebraic) Hamiltonians in the absence of magnetic fields.[25–29] The resulting X2C Hamiltonian and transformation matrices can then be expanded to obtain the expressions for NMS, SSC, and magnetizabilities.

[a]Author to whom correspondence should be addressed. Electronic mail: liuwj@pku.edu.cn.

II. THEORY

A. General formulation of two-component theory for second order magnetic properties

All equations are written in the System International based a.u. ($\hbar=m=e=1$, $c\approx 137$). The occupied, unoccupied, and arbitrary orbitals will be denoted as $i,j,\ldots,a,b,\ldots$, and $p,q,\ldots$, respectively. Plain and boldface capital letters refer respectively to operators and matrices. The Einstein summation convention over repeated indices is always employed. The Dirac equation for an electron reads

$$D\psi_p=\epsilon_p\psi_p,\quad D=c\vec{\alpha}\cdot\vec{\pi}+(\beta-1)c^2+V, \tag{1}$$

$$\vec{\pi}=\vec{p}+\vec{A}^{10}+\vec{A}^{01},\quad \vec{A}^{10}=\frac{1}{2}\vec{B}\times\vec{r},\quad \vec{A}^{01}=\frac{1}{c^2}\frac{\vec{\mu}\times\vec{r}}{r^3}, \tag{2}$$

where V is the nuclear Coulomb potential and $\vec{A}^{10}$ and $\vec{A}^{10}$ are the vector potentials due respectively to a uniform external magnetic field $\vec{B}$ and a nuclear magnetic point dipole moment $\vec{\mu}$. According to the generic ansatz of orbital decomposition,[20,30] the bispinors ψ_i can be expanded as[18]

$$\psi_p=\sum_\mu Z\begin{pmatrix} g_\mu\mathbf{A}_{\mu p}\\ \frac{1}{2c}\vec{\sigma}\cdot\vec{p}g_\mu\mathbf{B}_{\mu p}\end{pmatrix},\quad Z=\begin{pmatrix} Z_{11} & Z_{12}\\ Z_{21} & Z_{22}\end{pmatrix}. \tag{3}$$

The Z operator, for which various strictly equivalent choices[18,19] are possible, extends the $\vec{\sigma}\cdot\vec{p}$-basis to a field-dependent basis for the small component. Such an ansatz is equivalent to representing the effective Hamiltonian H and the nonunit metric S in the original $\vec{\sigma}\cdot\vec{p}$-basis, viz.,

$$H=Z^\dagger DZ,\quad S=Z^\dagger Z, \tag{4}$$

$$\begin{pmatrix}\mathbf{H}_{11} & \mathbf{H}_{12}\\ \mathbf{H}_{21} & \mathbf{H}_{22}\end{pmatrix}\begin{pmatrix}\mathbf{A}\\ \mathbf{B}\end{pmatrix}=\begin{pmatrix}\mathbf{S}_{11} & \mathbf{S}_{12}\\ \mathbf{S}_{21} & \mathbf{S}_{22}\end{pmatrix}\begin{pmatrix}\mathbf{A}\\ \mathbf{B}\end{pmatrix}\boldsymbol{\epsilon}, \tag{5}$$

where

$$(\mathbf{H}_{11})_{\mu\nu}=\langle g_\mu|Z_{11}^\dagger VZ_{11}+Z_{11}^\dagger c\vec{\sigma}\cdot\vec{\pi}Z_{21}+Z_{21}^\dagger c\vec{\sigma}\cdot\vec{\pi}Z_{11}+Z_{21}^\dagger(V-2c^2)Z_{21}|g_\nu\rangle, \tag{6}$$

$$(\mathbf{H}_{12})_{\mu\nu}=\frac{1}{2c}\langle g_\mu|Z_{11}^\dagger VZ_{12}+Z_{11}^\dagger c\vec{\sigma}\cdot\vec{\pi}Z_{22}+Z_{21}^\dagger c\vec{\sigma}\cdot\vec{\pi}Z_{12}+Z_{21}^\dagger(V-2c^2)Z_{22}|\vec{\sigma}\cdot\vec{p}g_\nu\rangle=(\mathbf{H}_{21})_{\nu\mu}^*, \tag{7}$$

$$(\mathbf{H}_{22})_{\mu\nu}=\frac{1}{4c^2}\langle\vec{\sigma}\cdot\vec{p}g_\mu|Z_{12}^\dagger VZ_{12}+Z_{12}^\dagger c\vec{\sigma}\cdot\vec{\pi}Z_{22}+Z_{22}^\dagger c\vec{\sigma}\cdot\vec{\pi}Z_{12}+Z_{22}^\dagger(V-2c^2)Z_{22}|\vec{\sigma}\cdot\vec{p}g_\nu\rangle, \tag{8}$$

$$(\mathbf{S}_{11})_{\mu\nu}=\langle g_\mu|Z_{11}^\dagger Z_{11}+Z_{21}^\dagger Z_{21}|g_\nu\rangle, \tag{9}$$

$$(\mathbf{S}_{12})_{\mu\nu}=\frac{1}{2c}\langle g_\mu|Z_{11}^\dagger Z_{12}+Z_{21}^\dagger Z_{22}|\vec{\sigma}\cdot\vec{p}g_\nu\rangle=(\mathbf{S}_{21})_{\nu\mu}^*, \tag{10}$$

$$(\mathbf{S}_{22})_{\mu\nu}=\frac{1}{4c^2}\langle\vec{\sigma}\cdot\vec{p}g_\mu|Z_{12}^\dagger Z_{12}+Z_{22}^\dagger Z_{22}|\vec{\sigma}\cdot\vec{p}g_\nu\rangle. \tag{11}$$

Equation (5) is the basis for the various four-component methods for NMS.[18,19] The aim here is to develop its two-component counterpart. By defining the following relationship between the small and large component expansion coefficients:

$$\mathbf{B}=\mathbf{XA}, \tag{12}$$

and invoking the same procedure as used for deriving the X2C Hamiltonians in the absence of magnetic fields,[25] we obtain

$$\mathbf{FA}=\tilde{\mathbf{S}}\mathbf{A}\boldsymbol{\epsilon},\quad \mathbf{A}^\dagger\tilde{\mathbf{S}}\mathbf{A}=\mathbf{I}, \tag{13}$$

$$\mathbf{F}=\mathbf{L}+\mathbf{X}^\dagger\overline{\mathbf{L}},\quad \mathbf{L}=\mathbf{H}_{11}+\mathbf{H}_{12}\mathbf{X},\quad \overline{\mathbf{L}}=\mathbf{H}_{21}+\mathbf{H}_{22}\mathbf{X}, \tag{14}$$

$$\tilde{\mathbf{S}}=\mathbf{M}+\mathbf{X}^\dagger\overline{\mathbf{M}},\quad \mathbf{M}=\mathbf{S}_{11}+\mathbf{S}_{12}\mathbf{X},\quad \overline{\mathbf{M}}=\mathbf{S}_{21}+\mathbf{S}_{22}\mathbf{X}. \tag{15}$$

The exact decoupling of Eq. (5) is only achieved if $\mathbf{X}$ satisfies the following implicity equation:

$$\mathbf{M}^{-1}\mathbf{L}=\overline{\mathbf{M}}^{-1}\overline{\mathbf{L}}\quad\text{or}\quad \mathbf{X}=\mathbf{H}_{22}^{-1}\overline{\mathbf{M}}\mathbf{M}^{-1}\mathbf{L}-\mathbf{H}_{22}^{-1}\mathbf{H}_{21}. \tag{16}$$

Equation (13) is the extension of the original NESC[16,25,26] to the case of magnetic fields. Other forms of $\mathbf{F}$ such as symmetrized elimination of the small component[28] are also possible but which will not be considered here. By setting $Z^{00}=1_4$, the zeroth order equations (original NESC) of Eqs. (13) and (16) are readily obtained as

$$\mathbf{F}^{00}\mathbf{A}^{00}=\tilde{\mathbf{S}}^{00}\mathbf{A}^{00}\boldsymbol{\epsilon}^{00}, \tag{17}$$

$$\mathbf{X}^{00}=\mathbf{I}+\frac{1}{4c^2}\mathbf{T}^{-1}\mathbf{W}\mathbf{X}^{00}-\frac{1}{2c^2}\mathbf{X}^{00}\mathbf{S}^{-1}\mathbf{L}^{00}, \tag{18}$$

where

$$\mathbf{F}^{00}=\mathbf{V}+\mathbf{T}\mathbf{X}^{00}+\mathbf{X}^{00\dagger}\mathbf{T}-\mathbf{X}^{00\dagger}\mathbf{T}\mathbf{X}^{00}+\frac{1}{4c^2}\mathbf{X}^{00\dagger}\mathbf{W}\mathbf{X}^{00}, \tag{19}$$

$$\tilde{\mathbf{S}}^{00}=\mathbf{S}+\frac{1}{2c^2}\mathbf{X}^{00\dagger}\mathbf{T}\mathbf{X}^{00}, \tag{20}$$

$$\mathbf{L}^{00}=\mathbf{V}+\mathbf{T}\mathbf{X}^{00}. \tag{21}$$

Here, $\mathbf{V}$ is the matrix of V, $\mathbf{T}$ is of the nonrelativistic kinetic operator T, and $\mathbf{W}$ of $\vec{\sigma}\cdot\vec{p}V\vec{\sigma}\cdot\vec{p}$ in the large component basis and $\boldsymbol{S}$ is the nonrelativistic metric. Equations (17) and (18) can be solved either iteratively or noniteratively.[25–28]

Without loss of generality, we can use the zeroth order spinors as the basis, in terms of which we have

$$\mathbf{A}^{00}=\mathbf{I},\quad \tilde{\mathbf{S}}^{00}=\mathbf{I},\quad \mathbf{F}^{00}=\epsilon^{00},\quad \mathbf{L}^{00}=\mathbf{S}\epsilon^{00},$$

$$\bar{\mathbf{L}}^{00}=\bar{\mathbf{M}}^{00}\epsilon^{00},\quad \bar{\mathbf{M}}^{00}=\mathbf{S}_{22}^{00}\mathbf{X}^{00},\quad \mathbf{S}_{22}^{00}=\frac{1}{2c^2}\mathbf{T}, \tag{22}$$

$$\bar{\mathbf{L}}^{00}=\mathbf{T}+\mathbf{H}_{22}^{00}\mathbf{X}^{00},\quad \mathbf{H}_{22}^{00}=\frac{1}{4c^2}\mathbf{W}-\mathbf{T}$$

Expanding Eqs. (13)–(16) to first and mixed second orders leads to

$$\mathbf{F}^{10}+\epsilon^{00}\mathbf{A}^{10}=\tilde{\mathbf{S}}^{10}\epsilon^{00}+\mathbf{A}^{10}\epsilon^{00}+\epsilon^{10}, \tag{23}$$

$$\mathbf{F}^{10}=\mathbf{H}_{11}^{10}+\mathbf{H}_{12}^{10}\mathbf{X}^{00}+\mathbf{X}^{00\dagger}(\mathbf{H}_{21}^{10}+\mathbf{H}_{22}^{10}\mathbf{X}^{00})+(\mathbf{X}^{10\dagger}\bar{\mathbf{L}}^{00}+\text{c.c.}) \tag{24}$$

$$\tilde{\mathbf{S}}^{10}=\mathbf{S}_{11}^{10}+\mathbf{S}_{12}^{10}\mathbf{X}^{00}+\mathbf{X}^{00\dagger}(\mathbf{S}_{21}^{10}+\mathbf{S}_{22}^{10}\mathbf{X}^{00})+(\mathbf{X}^{10\dagger}\bar{\mathbf{M}}^{00}+\text{c.c.}) \tag{25}$$

$$\mathbf{P}^{00}\mathbf{X}^{10}=\frac{1}{2c^2}\mathbf{X}^{10}\epsilon^{00}+\mathbf{Q}^{10},$$

$$\mathbf{P}^{00}=\frac{1}{4c^2}\mathbf{T}^{-1}\mathbf{W}-\mathbf{I}-\frac{1}{2c^2}\mathbf{X}^{00}\mathbf{S}^{-1}\mathbf{T},$$

$$\begin{aligned}\mathbf{Q}^{10}=&\frac{1}{2c^2}\mathbf{X}^{00}\mathbf{S}^{-1}[\mathbf{H}_{11}^{10}+\mathbf{H}_{12}^{10}\mathbf{X}^{00}-(\mathbf{S}_{11}^{10}+\mathbf{S}_{12}^{10}\mathbf{X}^{00})\epsilon^{00}]\\&-\mathbf{T}^{-1}[\mathbf{H}_{21}^{10}+\mathbf{H}_{22}^{10}\mathbf{X}^{00}-(\mathbf{S}_{21}^{10}+\mathbf{S}_{22}^{10}\mathbf{X}^{00})\epsilon^{00}],\end{aligned} \tag{26}$$

$$\begin{aligned}&\mathbf{F}^{11}+\mathbf{F}^{10}\mathbf{A}^{01}+\mathbf{F}^{01}\mathbf{A}^{10}+\epsilon^{00}\mathbf{A}^{11}\\&=\tilde{\mathbf{S}}^{10}\mathbf{A}^{01}\epsilon^{00}+\tilde{\mathbf{S}}^{01}\mathbf{A}^{10}\epsilon^{00}+\tilde{\mathbf{S}}^{11}\epsilon^{00}+\mathbf{A}^{11}\epsilon^{00}+\tilde{\mathbf{S}}^{01}\epsilon^{10}\\&+\mathbf{A}^{01}\epsilon^{10}+\tilde{\mathbf{S}}^{10}\epsilon^{01}+\mathbf{A}^{10}\epsilon^{01}+\epsilon^{11},\end{aligned} \tag{27}$$

$$\begin{aligned}\mathbf{F}^{11}=&\mathbf{H}_{11}^{11}+\mathbf{H}_{12}^{11}\mathbf{X}^{00}+\mathbf{X}^{00\dagger}\mathbf{H}_{21}^{11}+\mathbf{X}^{00\dagger}\mathbf{H}_{22}^{11}\mathbf{X}^{00}\\&+[(\mathbf{H}_{12}^{01}+\mathbf{X}^{00\dagger}\mathbf{H}_{22}^{01})\mathbf{X}^{10}+\text{c.c.}]+[\mathbf{X}^{01\dagger}\bar{\mathbf{L}}^{10}+\text{c.c.}]\\&+[\mathbf{X}^{11\dagger}\bar{\mathbf{L}}^{00}+\text{c.c.}]\end{aligned} \tag{28}$$

$$\begin{aligned}\tilde{\mathbf{S}}^{11}=&\mathbf{S}_{11}^{11}+\mathbf{S}_{12}^{11}\mathbf{X}^{00}+\mathbf{X}^{00\dagger}\mathbf{S}_{21}^{11}+\mathbf{X}^{00\dagger}\mathbf{S}_{22}^{11}\mathbf{X}^{00}\\&+[(\mathbf{S}_{12}^{01}+\mathbf{X}^{00\dagger}\mathbf{S}_{22}^{01})\mathbf{X}^{10}+\text{c.c.}]+[\mathbf{X}^{01\dagger}\bar{\mathbf{M}}^{10}+\text{c.c.}]\\&+[\mathbf{X}^{11\dagger}\bar{\mathbf{M}}^{00}+\text{c.c.}]\end{aligned} \tag{29}$$

$$\bar{\mathbf{L}}^{10}=\mathbf{H}_{21}^{10}+\mathbf{H}_{22}^{10}\mathbf{X}^{00}+\mathbf{H}_{22}^{00}\mathbf{X}^{10}, \tag{30}$$

$$\bar{\mathbf{M}}^{10}=\mathbf{S}_{21}^{10}+\mathbf{S}_{22}^{10}\mathbf{X}^{00}+\mathbf{S}_{22}^{00}\mathbf{X}^{10}. \tag{31}$$

Replacing the superscripts "10" with "01" in Eqs. (23)–(26) leads to the corresponding expressions for ϵ^{01}, $\mathbf{F}^{01}$, $\tilde{\mathbf{S}}^{01}$, and $\mathbf{X}^{01}$, respectively. After some straightforward algebra, we finally obtain the mixed second order energy as

$$E^{11}=E^{D}+E^{P0}+E^{P1}+E^{P2}, \tag{32}$$

where

$$\begin{aligned}E^{D}=&(\mathbf{H}_{11}^{11}+\mathbf{H}_{12}^{11}\mathbf{X}^{00}+\mathbf{X}^{00\dagger}\mathbf{H}_{21}^{11}+\mathbf{X}^{00\dagger}\mathbf{H}_{22}^{11}\mathbf{X}^{00})_{ii}\\&-(\mathbf{S}_{11}^{11}+\mathbf{S}_{12}^{11}\mathbf{X}^{00}+\mathbf{X}^{00\dagger}\mathbf{S}_{21}^{11}+\mathbf{X}^{00\dagger}\mathbf{S}_{22}^{11}\mathbf{X}^{00})_{ii}\epsilon_i^{00},\end{aligned} \tag{33}$$

$$\begin{aligned}E^{P0}=&-(\mathbf{H}_{11}^{01}+\mathbf{H}_{12}^{01}\mathbf{X}^{00}+\mathbf{X}^{00\dagger}\mathbf{H}_{21}^{01}+\mathbf{X}^{00\dagger}\mathbf{H}_{22}^{01}\mathbf{X}^{00})_{ij}\tilde{\mathbf{S}}_{ji}^{10}\\&+(\mathbf{S}_{11}^{01}+\mathbf{S}_{12}^{01}\mathbf{X}^{00}+\mathbf{X}^{00\dagger}\mathbf{S}_{21}^{01}+\mathbf{X}^{00\dagger}\mathbf{S}_{22}^{01}\mathbf{X}^{00})_{ij}\tilde{\mathbf{S}}_{ji}^{10}\epsilon_i^{00},\end{aligned} \tag{34}$$

$$\begin{aligned}E^{P1}=&[(\mathbf{H}_{11}^{01}+\mathbf{H}_{12}^{01}\mathbf{X}^{00}+\mathbf{X}^{00\dagger}\mathbf{H}_{21}^{01}+\mathbf{X}^{00\dagger}\mathbf{H}_{22}^{01}\mathbf{X}^{00})_{ia}\mathbf{A}_{ai}^{10}\\&+\text{c.c.}]-[(\mathbf{S}_{11}^{01}+\mathbf{S}_{12}^{01}\mathbf{X}^{00}+\mathbf{X}^{00\dagger}\mathbf{S}_{21}^{01}\\&+\mathbf{X}^{00\dagger}\mathbf{S}_{22}^{01}\mathbf{X}^{00})_{ia}\mathbf{A}_{ai}^{10}\epsilon_i^{00}+\text{c.c.}],\end{aligned} \tag{35}$$

$$\begin{aligned}E^{P2}=&[((\mathbf{H}_{12}^{01}+\mathbf{X}^{00\dagger}\mathbf{H}_{22}^{01})\mathbf{X}^{10})_{ii}+\text{c.c.}]-[((\mathbf{S}_{12}^{01}\\&+\mathbf{X}^{00\dagger}\mathbf{S}_{22}^{01})\mathbf{X}^{10})_{ii}\epsilon_i^{00}+\text{c.c.}]-(\mathbf{S}_{11}^{01}+\mathbf{S}_{12}^{01}\mathbf{X}^{00}\\&+\mathbf{X}^{00\dagger}\mathbf{S}_{21}^{01}+\mathbf{X}^{00\dagger}\mathbf{S}_{22}^{01}\mathbf{X}^{00})_{ii}\epsilon_i^{10},\quad \epsilon_i^{10}=F_{ii}^{10}-\tilde{\mathbf{S}}_{ii}^{10}\epsilon_i^{00}.\end{aligned} \tag{36}$$

It is seen that quantities such as $\mathbf{A}^{01}$ and $\mathbf{X}^{01}$ are not needed for the mixed second order energy, in line with the Dalgarno interchange theorem for double perturbations. The correspondence between the two- and four-component dia- and paramagnetic terms will be analyzed elsewhere. Although we have mainly NMS in mind, the above formulation can also be used to derive expressions specific to SSC or magnetizability.

B. Two–component external field-dependent unitary transformation (2c-EFUT) for NMS

As an application of the previous general formulation, we now consider the EFUT ansatz for NMS. Other schemes such as the orbital decomposition approach and restricted magnetic balance[18,19] will be presented elsewhere. Specifically,

$$Z^{00}=1_4,\quad Z^{01}=0_4,\quad Z^{10}=\begin{pmatrix}0 & -\frac{1}{2c}\vec{\sigma}\cdot\vec{A}^{10}\\ \frac{1}{2c}\vec{\sigma}\cdot\vec{A}^{10} & 0\end{pmatrix}, \tag{37}$$

where the second equality implies that the (singular) vector potential $\vec{A}^{01}$ is not transformed. Otherwise, special care must be taken of the numerical instabilities.[18] Equation (37) leads to the following structure for the four-component matrices:

$$\begin{aligned}&\mathbf{S}^{10}=\mathbf{S}^{01}=\mathbf{S}^{11}=0_4,\quad \mathbf{H}^{10}=\begin{pmatrix}\mathbf{H}_{11}^{10} & 0\\ 0 & \mathbf{H}_{22}^{10}\end{pmatrix},\\&\mathbf{H}^{01}=\begin{pmatrix}0 & \mathbf{H}_{12}^{01}\\ \mathbf{H}_{21}^{01} & 0\end{pmatrix},\quad \mathbf{H}^{11}=\begin{pmatrix}\mathbf{H}_{11}^{11} & 0\\ 0 & \mathbf{H}_{22}^{11}\end{pmatrix},\end{aligned} \tag{38}$$

where

$$(\mathbf{H}_{11}^{10})_{\mu\nu} = \tfrac{1}{2}\langle g_\mu|\vec{\sigma}\cdot\vec{p}\vec{\sigma}\cdot\vec{A}^{10} + \vec{\sigma}\cdot\vec{A}^{10}\vec{\sigma}\cdot\vec{p}|g_\nu\rangle, \tag{39}$$

$$(\mathbf{H}_{22}^{10})_{\mu\nu} = -\tfrac{1}{8c^2}\langle\vec{\sigma}\cdot\vec{p}g_\mu|\vec{\sigma}\cdot\vec{p}\vec{\sigma}\cdot\vec{A}^{10} + \vec{\sigma}\cdot\vec{A}^{10}\vec{\sigma}\cdot\vec{p}|\vec{\sigma}\cdot\vec{p}g_\nu\rangle, \tag{40}$$

$$(\mathbf{H}_{12}^{01})_{\mu\nu} = \tfrac{1}{2}\langle g_\mu|\vec{\sigma}\cdot\vec{A}^{01}\vec{\sigma}\cdot\vec{p}|g_\nu\rangle, \tag{41}$$

$$(\mathbf{H}_{21}^{01})_{\mu\nu} = \tfrac{1}{2}\langle g_\mu|\vec{\sigma}\cdot\vec{p}\vec{\sigma}\cdot\vec{A}^{01}|g_\nu\rangle, \tag{42}$$

$$(\mathbf{H}_{11}^{11})_{\mu\nu} = \langle g_\mu|\vec{A}^{01}\cdot\vec{A}^{10}|g_\nu\rangle, \tag{43}$$

$$(\mathbf{H}_{22}^{11})_{\mu\nu} = -\frac{1}{4c^2}\langle\vec{\sigma}\cdot\vec{p}g_\mu|\vec{A}^{01}\cdot\vec{A}^{10}|\vec{\sigma}\cdot\vec{p}g_\nu\rangle. \tag{44}$$

The general equations (24)–(26) in Sec. II A are then simplified to

$$\mathbf{F}^{10} = \mathbf{H}_{11}^{10} + \mathbf{X}^{00\dagger}\mathbf{H}_{22}^{10}\mathbf{X}^{00} + (\mathbf{X}^{10\dagger}\bar{\mathbf{L}}^{00} + \text{c.c.}), \tag{45}$$

$$\tilde{\mathbf{S}}^{10} = \frac{1}{2c^2}\mathbf{X}^{10\dagger}\mathbf{T}\mathbf{X}^{00} + \text{c.c.}, \tag{46}$$

$$\mathbf{P}^{00}\mathbf{X}^{10} = \frac{1}{2c^2}\mathbf{X}^{10}\boldsymbol{\epsilon}^{00} + \mathbf{Q}^{10},$$

$$\mathbf{P}^{00} = \frac{1}{4c^2}\mathbf{T}^{-1}\mathbf{W} - \mathbf{I} - \frac{1}{2c^2}\mathbf{X}^{00}\mathbf{S}^{-1}\mathbf{T}, \tag{47}$$

$$\mathbf{Q}^{10} = \frac{1}{2c^2}\mathbf{X}^{00}\mathbf{S}^{-1}\mathbf{H}_{11}^{10} - \mathbf{T}^{-1}\mathbf{H}_{22}^{10}\mathbf{X}^{00}.$$

Equation (47) suggests an iterative scheme starting from zeroing the first term on the right hand side. Typically it takes only two or three iterations to achieve convergence. A noniterative scheme is obtained by rewriting Eq. (47) in a basis that diagonalizes the matrix $\mathbf{P}^{00}$, viz.,

$$\mathbf{P}^{00}\mathbf{z} = \mathbf{z}\lambda, \quad \lambda(\mathbf{z}^{-1}\mathbf{X}^{10}) = \frac{1}{2c^2}(\mathbf{z}^{-1}\mathbf{X}^{10})\boldsymbol{\epsilon}^{00} + \mathbf{z}^{-1}\mathbf{Q}^{10},$$

$$\mathbf{X}_{pq}^{10} = \sum_r \mathbf{z}_{pr}\left(\lambda_r - \frac{1}{2c^2}\epsilon_q^{00}\right)^{-1}(\mathbf{z}^{-1}\mathbf{Q}^{10})_{rq}. \tag{48}$$

The $\{\mathbf{A}_{ai}^{10}\}$ can then be obtained from Eqs. (23), (45), and (46). The terms in Eq. (32) now read

$$E^D = (\mathbf{H}_{11}^{11} + \mathbf{X}^{00\dagger}\mathbf{H}_{22}^{11}\mathbf{X}^{00})_{ii}, \tag{49}$$

$$E^{P0} = -(\mathbf{H}_{12}^{01}\mathbf{X}^{00} + \mathbf{X}^{00\dagger}\mathbf{H}_{21}^{01})_{ij}\tilde{\mathbf{S}}_{ji}^{10}, \tag{50}$$

$$E^{P1} = (\mathbf{H}_{12}^{01}\mathbf{X}^{00} + \mathbf{X}^{00\dagger}\mathbf{H}_{21}^{01})_{ia}\mathbf{A}_{ai}^{10} + \text{c.c.}, \tag{51}$$

$$E^{P2} = (\mathbf{H}_{12}^{01}\mathbf{X}^{10} + \mathbf{X}^{10\dagger}\mathbf{H}_{21}^{01})_{ii}. \tag{52}$$

The above 2c-EFUT is completely equivalent to the four–component counterpart, 4c-EFUT[18,19] for any finite basis. When the basis is complete, the results will be the same as those by the exact analytical expression[19]. Such an equivalence is confirmed also by (uncoupled) calculations on neutral rare-gas atoms.

III. CONCLUSIONS

It has been demonstrated that the matrix formulation of two-component theory for NMR parameters is not only exact but also simple. The generalization to many-electron systems, including the proper treatment of distributed gauges, is straightforward. The efficiency and the corrections for two-electron picture change errors will be attained via the idea of "from atoms to molecule."[27,28] In view of the ease, the previous quasirelativistic theories have become essentially obsolete.

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