A point-charge model for the nuclear quadrupole moment: Coupled-cluster, Dirac–Fock, Douglas–Kroll, and nonrelativistic Hartree–Fock calculations for the Cu and F electric field gradients in CuF

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A point charge model for the nuclear quadrupole moment tensor (PCNQM) is developed in order to determine accurate electric field gradients (EFG) at the relativistic and correlated levels. The symmetric s contributions arising from the Poisson equation are avoided by using an appropriate point charge distribution in three-dimensional space. It is shown that the PCNQM model yields virtually the same EFGs compared to the conventional method of expectation values, if the point charges are set at small displacements from the nucleus ($d < 10^{-13}$ m) and the SCF energy is converged out to 12 significant figures. We further demonstrate that the choice of the point charge ζ is not very critical to the PCNQM perturbation, and that the correlation energy at both the nonrelativistic and relativistic level of theory depends linearly on ζ. This suggests that accurate EFG tensors can be obtained by performing only two correlated calculations for each atom and tensor component. The PCNQM model is tested on one-electron atoms and on the Cu and F EFG in CuF. Relativistic and correlation effects on EFGs are discussed in detail. A Z-expansion on one-electron systems demonstrates that the relativistic correction scales $\sim Z^5$. For the CuF molecule Douglas–Kroll and Dirac–Fock coupled cluster calculations are in good agreement with each other. At the best level of theory (coupled cluster Dirac–Fock plus correction from basis set incompleteness) we obtain a nuclear quadrupole coupling constant for ^{63}Cu of 23 Mhz. This is in very good agreement with the experimental result of 22 MHz considering the large standard deviation of the ^{63}Cu nuclear quadrupole moment applied, 220(10) mb.   © *1998 American Institute of Physics.* [S0021-9606(98)02415-5]

I. INTRODUCTION

In the multipole expansion of the interaction between two charge distributions,[1] the electric field gradient (EFG) of the charge distribution ϱ_1 interacts with the second moment of the nuclear charge distribution ϱ_2, the (electric) nuclear quadrupole moment (NQM). The EFG tensor at a nucleus is very sensitive to slightly varying electron distributions in the near vicinity of the nucleus.[2] Therefore, EFGs are useful for the investigation of weakly bound complexes and can act as an indicator for small external perturbations like solvent effects.[3,4] EFGs also play an important role in the determination of NQMs from spectroscopic hyperfine coupling.[5–16] An accurate determination of the EFG at the location of the nucleus is therefore desirable. Since the EFG scales $\sim r^{-3}$, it is an inner shell property and one may expect significant contributions from relativistic effects and electron correlation.[17–19]

In the nonrelativistic case the EFGs for atoms and molecules can be obtained straightforwardly by computation of the expectation value over the EFG operator. For atoms and a few diatomic molecules containing light atoms accurate SCF wave functions can be obtained by discretization methods[20–30] where for systems with lower symmetry the

algebraic approach is well established. Furthermore, even for most of the nonrelativistic electron correlation methods the coupled-perturbed wave functions are available and provide an efficient route to evaluate the analytic properties.

On the other hand changing to heavier elements makes a relativistic treatment inevitable and to our knowledge no analytic calculation at the four-component level is implemented yet. Especially the correlation treatment at the four-component level is very expensive and currently not feasible for larger molecules and an alternative method for EFG calculations instead of an analytical treatment is desirable. In the cases where a picture change[31–33] is applied to treat relativistic effects as in the Douglas–Kroll scheme,[34–36] an appropriate relativistic transformation of the EFG operator becomes necessary as well. In contrast to the Coulomb operator the transformation of the EFG operator is complicated and cumbersome. The evaluation of EFG matrix elements using transformed wave functions only without transforming the operator, e.g., the Douglas–Kroll[34–36] or other transformations, may lead to substantial deviations in the EFG.[37]

Electron correlation and relativistic effects can also be taken into account by the use of a multiple perturbation expansion.[10,12,15,17,19] The one-electron relativistic corrections and correlation contributions are hereby considered as internal (formal) perturbations where the external perturbation causes a linear response in the molecule yielding the

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desired kth order property $Q^{(k)}$. The multiple perturbation expansion is written as

$$E = E(\lambda,\mu,\sigma) = \sum_{k,m,n} E^{(k,m,n)} = \sum_k c_k Q^{(k,m,n)}. \qquad (1)$$

λ,μ,σ are the perturbation parameters for the external perturbation, the relativistic correction and the correlation contribution. Differentiation of the calculated total electronic energies with respect to λ, μ, and σ yields the corresponding contributions to the kth order properties. However, the one-electron relativistic effects are only treated as low order corrections to the energy and changes in the wave function might also be important. The multiple perturbation expansion was applied to various molecules using the Pauli relativistic Hamiltonian (mass-velocity and Darwin term)[38] in connection with a subsequent MBPT or CCSD(T) calculation.[15,17]

The lack of the appropriate treatment of analytic properties in relativistic methods motivates a model of general applicability and without any restrictions concerning the complexity of the wave function.

In the next section we outline the point charge model for the NQM which we denote as the PCNQM model. In order to establish if this model works, we performed one-electron Hartree–Fock (HF) calculations on a series of atoms with different nuclear charges Z (up to $Z=85$) and varying NQMs. The PCNQM model is then compared with the conventional method over expectation values. In the last section we perform PCNQM calculations on CuF using large basis sets including both relativistic and correlation effects.

II. THE POINT CHARGE MODEL FOR THE NQM

We briefly review some important aspects on EFGs which are necessary for the discussion of our proposed point charge model. The components of the electronic and nuclear field gradient tensor $q^{el}_{\alpha\beta}$ and $q^{nuc}_{\alpha\beta}$ at nucleus X are the expectation values over the corresponding operators[39]

$$\hat{q}^{el}_{\alpha\beta}(\mathbf{R}_X) = \sum_i^n \frac{3(r_{i\alpha}-R_{X\alpha})(r_{i\beta}-R_{X\beta}) - \delta_{\alpha\beta}|\mathbf{r}_i-\mathbf{R}_X|^2}{|\mathbf{r}_i-\mathbf{R}_X|^5} \qquad (2)$$

and

$$\hat{q}^{nuc}_{\alpha\beta}(\mathbf{R}_X) = \sum_{Y\neq X} \frac{Z_X[3(R_{Y\alpha}-R_{X\alpha})(R_{Y\beta}-R_{X\beta}) - \delta_{\alpha\beta}|\mathbf{R}_X-\mathbf{R}_Y|^2]}{|\mathbf{R}_X-\mathbf{R}_Y|^5} \qquad (3)$$

within the Born–Oppenheimer approximation.[40] In expressions (2) and (3) α,β stand for x,y or z, $(x,y,z)=\mathbf{r}_\alpha$ and $(X,Y,Z)=\mathbf{R}_\alpha$; the summation in (2) runs over all electrons i and the summation in (3) runs over all nuclei X. $\langle \hat{q}^{el}_{zz} \rangle = q^{el}_{zz}$ can be obtained by differentiating twice the potential of the charge distribution $\varrho = |\Psi|^2$ with respect to the Cartesian coordinates of the point (R_{Xx},R_{Xy},R_{Xz}):

$$q^{el}_{\alpha\beta}(\mathbf{R}_X,\Psi) = \langle \Psi(\mathbf{r}_1,\ldots,\mathbf{r}_n) | \frac{\partial^2}{\partial R_{X\alpha} \partial R_{X\beta}}$$

$$\times \sum_i^n \frac{1}{|\mathbf{r}_i-\mathbf{R}_X|} | \Psi(\mathbf{r}_1,\ldots,\mathbf{r}_n) \rangle. \qquad (4)$$

If $\Psi(\mathbf{r}_1,\ldots,\mathbf{r}_n)$ can be represented as an antisymmetric product of one-particle functions $\phi_i(\mathbf{r})$ (Hartree–Fock case; HF) the expression (4) can be written as a sum of one-particle integrals of the form

$$q^{el}_{\alpha\beta}(\mathbf{R}_X,\phi_i^{HF}) = \sum_i^n \langle \phi_i(\mathbf{r}) | \frac{\partial^2}{\partial R_{X\alpha} \partial R_{X\beta}} \frac{1}{|\mathbf{r}-\mathbf{R}_X|} | \phi_i(\mathbf{r}) \rangle. \quad (5)$$

After transformation into spherical coordinates the evaluation of (5) for s-type Gaussian basis functions leads to a zero (angular part) times infinity (radial part) case at the origin. This situation can easily be avoided by either neglecting the s contributions completely (since only the traceless EFG tensor is needed), or by interchanging the order of integration and differentiation followed by a subsequent Gaussian transformation of the potential operator.[41] In the latter case, the higher angular momentum functions can then be obtained recursively by modern schemes of integral evaluation.[42] Both procedures are in use in standard quantum chemical software packages.[43,44]

The interaction energy U between an arrangement of point charges e_i simulating the NQM and a potential $\phi(\mathbf{r})$ coming from a charge distribution $\varrho(\mathbf{r})$ can be written as a Taylor expansion

$$U = U_0 + \sum_i e_i \left\{ \phi_0 + \frac{\partial\phi}{\partial r_\alpha}\bigg|_0 r_{i\alpha} + \frac{1}{2}\frac{\partial^2\phi}{\partial r_\alpha \partial r_\beta}\bigg|_0 r_{i\alpha} r_{i\beta} + \cdots \right\}. \qquad (6)$$

The Einstein notation for summation is used. With the definitions for the electric field $\mathbf{E}$ and the field gradient $F^{\alpha\beta}$

$$\mathbf{E} = -\nabla\phi \quad \text{and} \quad F^{\alpha\beta} = \frac{\partial E^\alpha}{\partial\beta} = -\frac{\partial^2\phi}{\partial r_\alpha \partial r_\beta} \qquad (7)$$

we obtain the expression up to second order[45]

$$U = U_0 + q_{tot}\,\phi_0 - \mu_\alpha E^\alpha - \tfrac{1}{2}Q_{\alpha\beta}F^{\alpha\beta}. \qquad (8)$$

μ_α is the Cartesian component of the dipole moment and $Q_{\alpha\beta}$ is the quadrupole moment of the e_i arrangement:

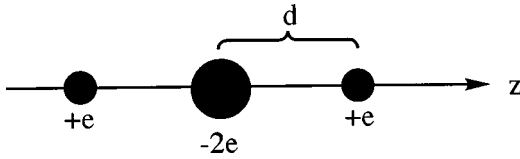$$Q_{\alpha\beta} = \sum_i e_i r_{i\alpha} r_{i\beta}. \qquad (9)$$

FIG. 1. Point charge model for the NQM.

The common notation for the zz component of the EFG tensor is $q_{zz} = (\partial^2 \phi / \partial z^2)$ and is the negative of F^{zz} which sometimes causes confusion in the sign of the EFG components.[46,47] If not otherwise mentioned, we use q_{zz} instead of q_{zz}^{el}. The term $q_{tot}\phi_0$ is contained in the molecular Hamiltonian, and the tensor product $U_{int} = -\frac{1}{2}Q_{\alpha\beta}F^{\alpha\beta}$ represents the small additional interaction energy between the nuclear quadrupole and the field gradient. There is (currently) no measurable nuclear dipole moment which could interact with the electric field of the charge distribution $\varrho(\mathbf{r})$.

To vary the total energy as a consequence of the EFG-quadrupole perturbation U_{int}, we generate an artificial "quadrupole moment" by placing additional point charges ζ_i at a distance of d around the nucleus (d should not be much larger than the size of the nucleus, i.e., $d < 10^{-3}$ a.u.). We can use the following arrangement shown in most nuclear physics textbooks, Fig. 1.[48] The general expression of the interaction energy

$$U_{int} = \frac{1}{2} \sum_i \zeta_i r_{i\alpha} r_{i\beta} \left(\frac{\partial^2 \phi}{\partial r_\alpha \partial r_\beta} \right) \tag{10}$$

simplifies for the arrangement of Fig. 1 to

$$U_{int} = \frac{1}{2}(\zeta d^2 q_{zz} + \zeta(-d)^2 q_{zz}) = Q q_{zz}, \tag{11}$$

where the abbreviation $Q = \zeta d^2$ was used. The total charge remains conserved for all Q.

Variation of Q causes a change in the total electronic energy E and the expectation value $q_{zz}|_0$ can therefore be obtained. Compared to the Coulomb energy, U_{int} is quite small so that the perturbational ansatz

$$\hat{H}(Q) = \hat{H}_0 + Q q_{zz} \tag{12}$$

for the total Hamiltonian is justified,

$$\hat{H}(Q)\Psi(Q) = E(Q)\Psi(Q), \quad \langle\Psi(Q)|\Psi(Q)\rangle = 1, \tag{13}$$

$$E(Q) = \langle\Psi(Q)|\hat{H}(Q)|\Psi(Q)\rangle. \tag{14}$$

The energy with quadrupole perturbation can be expanded as

$$E(Q) = E_0 + Q\left(\frac{dE(Q)}{dQ}\right)_0 + \frac{Q^2}{2}\left(\frac{d^2E(Q)}{dQ^2}\right)_0 + \dots, \tag{15}$$

with the first-order response

$$E_1 = \left(\frac{dE(Q)}{dQ}\right)_0. \tag{16}$$

At this stage $E(Q) = \langle\Psi(Q)|\hat{H}(Q)|\Psi(Q)\rangle$ can be calculated to every desired accuracy taking electron correlation and relativistic effects into account. Differentiating (14) with respect to Q and taking the Hellmann–Feynman theorem into account yields

$$\left.\frac{dE(Q)}{dQ}\right|_0 = \langle\Psi(Q=0)|q_{zz}|\Psi(Q=0)\rangle. \tag{17}$$

Hence numerical differentiation of the perturbed energy calculated with an arbitrary complex wave function leads to the expectation value of the EFG operator containing the corresponding contributions at a uniform level of treatment. A small advantage of our PCNQM method over the conventional expectation value method is that the Hellmann–Feynman-type errors are avoided. The first-order response in Eq. (15) will be analyzed for the molecular calculations on CuF.

III. ATOMIC CALCULATIONS

Introducing a fixed axis, q_{zz} can be written as

$$q_{zz}(\mathbf{R}=0) = \langle\Psi| \sum_i \frac{3\cos^2\theta_i - 1}{r_i^3} |\Psi\rangle, \tag{18}$$

where θ is the angle between the point of consideration and the axis. In the case of a one-electron atom in the state Ψ_{nlm} an analytical nonrelativistic expression for the EFG at the nucleus can be given for $l > 0$;[2]

$$q(\Psi_{nlm})|_0 = \frac{l(l+1) - 3m^2}{(l-\frac{1}{2})(2l+3)} \langle r^{-3}\rangle, \tag{19}$$

where the nonrelativistic expression for $\langle r^{-3}\rangle$ is

$$\langle r^{-3}\rangle = \frac{Z^3}{n^3 l(l+\frac{1}{2})(l+1)}. \tag{20}$$

Since the EFG operator behaves like $1/r^3$ large relativistic effects are to be expected. For the relativistic case closed-form expressions for the diagonal r^k expectation values are also known[49–51] and convenient expressions for $-6 \leq k \leq 5$ were recently given by Andrae.[52] Concerning only the radial part of the EFG expectation value one can estimate the relativistic corrections to $\langle r^{-3}\rangle$. The relativistic formula due to Ref. 52 is

$$\langle r^{-3}\rangle = (2Z)^3 \frac{6\kappa^2(n_r + \gamma)^2 + 2N^2(1 - \gamma^2) - 6N\kappa(n_r + \gamma)}{N^5(2\gamma - 2)(2\gamma - 1)2\gamma(2\gamma + 1)(2\gamma + 2)}$$

$$= (2Z)^3 f\left(\frac{Z}{c}\right), \tag{21}$$

where κ is the relativistic quantum number, $n_r = n - |\kappa|$, $\gamma = \sqrt{\kappa^2 - (Z/c)^2}$ and $N = \sqrt{n_r^2 + 2n_r\gamma + \kappa^2}$. If one expands this expression with the respect to (Z/c) one yields

$$\langle r^{-3}\rangle = Z^3\left(8f(0) + 8f'(0)\frac{Z}{c} + 4f''(0)\left(\frac{Z}{c}\right)^2 + \dots\right), \tag{22}$$

where

$$f(0) = \begin{cases} (n^3 2\kappa(2\kappa+1)(2\kappa+2))^{-1} & \kappa > 0 \\ (n^3 2|\kappa|(2|\kappa|-1)(2|\kappa|-2))^{-1} & \kappa < 0 \end{cases}, \tag{23}$$

$$f'(0) = 0, \tag{24}$$

and

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$$f''(0) = \frac{1}{n^5 g(|\kappa|)|\kappa|} \{ -4|\kappa|(n+|\kappa|)^2 + 8n^2|\kappa| - 4(n-|\kappa|)$$

$$+ 12n\kappa - 6|\kappa|\kappa\} - \frac{(2\kappa-1)(2\kappa-2)}{n^5 g^2(|\kappa|)} \left\{ n^2 \left(120|\kappa| \right. \right.$$

$$\left. \left. -160|\kappa|^3 - \frac{8}{|\kappa|} \right) - \frac{5(n-|\kappa|)}{|\kappa|} g(|\kappa|) \right\}, \qquad (25)$$

with $g(|\kappa|) = 32|\kappa|^5 - 40|\kappa|^3 + 8|\kappa|$. Inserting the values for a specific l-dependent function into the leading term yields exactly the nonrelativistic expectation value given in Eq. (20). We therefore conclude that relativistic effects scale like Z^5 and large relativistic changes in EFGs are expected for heavy atoms, as has been pointed out earlier on an empirical basis.[53] For κ of a $2p_{1/2}$ function ($\kappa = 1 = l$) and of a $2p_{3/2}$ function ($\kappa = -2 = -l-1$) the nonrelativistic value of a $2p$ function is $Z^3/24$. The second-order correction factor for a $2p_{3/2}$ function is $4f''_{P_{3/2}}(0) = 2.256\,944\,44 \times 10^{-2}$. Note that the expectation values shown above contain only the radial part of the wave function.

In order to show that the PCNQM model shown in Fig. 1 performs well, we carried out a series of nonrelativistic atomic one-electron calculations on the 1^2S and 2^2P states. A even-tempered basis sets of $28s$ (for the 1^2S state) and $28 p$ functions (for the 2^2P state) was used starting at exponent 0.0064 and applying a scaling factor of 2.0. In the case of an s function, which has a nonvanishing density at the nucleus, one should obtain a contribution to the EFG within the PC-NQM model shown in Fig. 1. The EFG at $\mathbf{R} = 0$ of a Gauss-type $1s$ function located at the origin is

$$q_{zz}(\mathbf{R} = 0, 1s) = \lim_{\mathbf{R} \to 0} \int \Psi^*_{1s}(\mathbf{r}) \frac{\partial^2}{\partial R_z^2} \frac{1}{|\mathbf{r} - \mathbf{R}|} \Psi_{1s}(\mathbf{r}) d\mathbf{r}. \qquad (26)$$

Performing the limiting process before the integration will cause mathematical difficulties as mentioned in the introduction. Therefore, the integral with respect to $\mathbf{r}$ is evaluated first and the limiting process is performed after the differentiation of the resulting expression. In the case of a normalized $1s$ Gaussian function

$$\Psi(\mathbf{r}) = \left(\frac{2\alpha}{\pi} \right)^{3/4} e^{-\alpha r^2} \qquad (27)$$

this leads to a $q_{zz}|_0$ value of

$$q_{zz}|_0 = \lim_{\mathbf{R} \to 0} \frac{\partial^2}{\partial R_z^2} \sqrt{\frac{8\alpha}{\pi}} \int_0^1 \exp\{-2\alpha|\mathbf{R}|^2 t^2\} dt$$

$$= \frac{8}{3} \sqrt{\frac{2\alpha^3}{\pi}}. \qquad (28)$$

The nontraceless diagonal components are implemented in GAUSSIAN94.[43] In the case of an exponent of $\alpha = 0.4$ we obtain
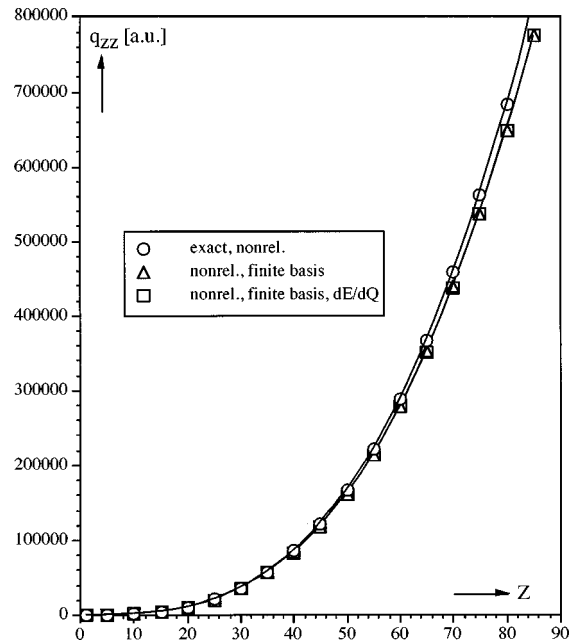
$$q_{zz}|_0 = 0.538\,268\,271 \qquad (29)$$

FIG. 2. The $1s$ Poisson contribution to the EFG for one-electron atoms up to a nuclear charge of $Z = 85$. A distance of $d = 10^{-3}$ a.u. was chosen for the PCNQM model shown in Fig. 1.

which is consistent with Eq. (28). Due to the symmetry for s-type functions the field may also be applied in x or y direction yielding the same value for q_{xx} and q_{yy}. In other words,

$$q_{xx} = q_{yy} = q_{zz} \qquad (30)$$

which verifies the Poisson equation at the origin:

$$\langle \Delta\phi \rangle(\mathbf{R} = 0) = q_{xx}|_0 + q_{yy}|_0 + q_{zz}|_0$$

$$= -4\pi\varrho(\mathbf{R} = 0)$$

$$= -\text{tr}(\mathbf{F}) = 4\pi \left(\frac{2\alpha}{\pi} \right)^{3/2} \overset{\alpha = 0.4}{=} 1.614\,804\,8. \qquad (31)$$

ϱ is the charge density. In the extension to a complete basis set this value approaches $\frac{4}{3}Z^3$. These spherical contributions can be quite large compared to the p contributions, and may cause numerical difficulties in the transformation to the traceless tensor. Since they are independent of the nuclear orientation they do not contribute to the energy shift due to the NQMs. The EFG-tensor $\mathbf{F}$ is often transformed to a traceless form which can be achieved by subtracting the spherical tensor $\mathbf{K} = \frac{1}{3}\text{tr}(\mathbf{F})$ from $\mathbf{F}$. The remaining tensor contains only nonspherical parts contributing to the energy shift and is called the deviator. In this case the Laplace equation is satisfied, because $\varrho(0) = 0$ for all functions $l > 0$. One easily sees that for a $1s$ function the diagonal elements of $\mathbf{F} - \mathbf{K}$ vanish.

Figure 2 shows the s-contributions obtained from our PCNQM model in comparison with the one derived from the expectation value, and the exact formula given by the Poisson equation for a hydrogenlike $1s$ function. For the PC-NQM calculations we used $d = 10^{-4}$ a.u. and chose the charges $\zeta \in \{+0.2, +0.1, 0, -0.1, -0.2\}$ a.u. The EFGs are obtained by numerical differentiation.
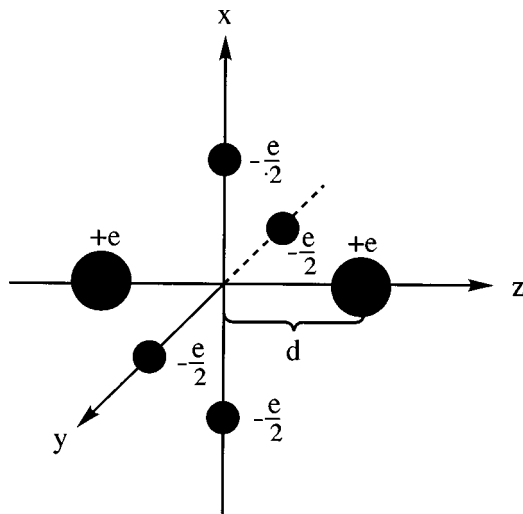
FIG. 3. Point charge model in three-dimensional space for the NQM annihilating contributions from s functions.
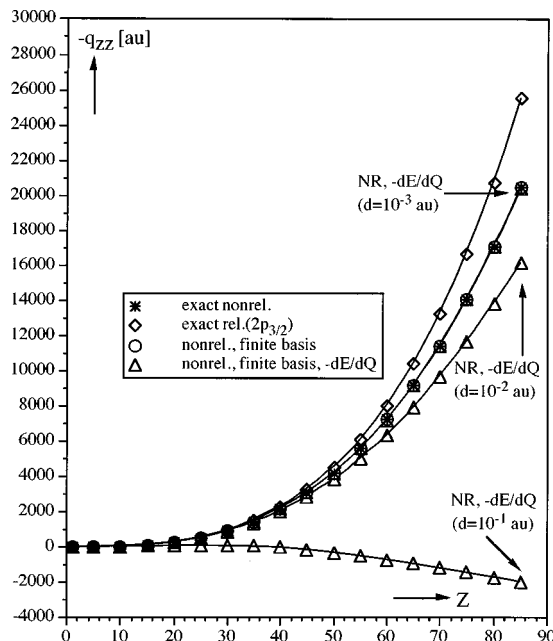

FIG. 4. The $2p$ contribution to the EFG for one-electron atoms up to a nuclear charge of $Z=85$ applying different distances d (see Fig. 1). The graph also shows the exact nonrelativistic and relativistic ($2p_{3/2}$) EFG for comparison.

The PCNQM results are in very good agreement with the results obtained from the expectation value over the EFG operator. For example, for $Z=50$ we obtain $q_{zz}=161\,549$ a.u. compared to the expectation value of $161\,507$ a.u. The difference is due to the numerical accuracy of the PCNQM method. Note that the NQM is of the order of 10^{-9} a.u. In order to obtain better results, a smaller distance d should be chosen and the integral accuracy has to be improved beyond 10^{-12} a.u. At this stage we note that a relativistic calculation for the s contribution using a nuclear point charge model will lead to a singular result at $r=0$, because the electron density of a Dirac $1s_{1/2}$ function is

$$\varrho(|\mathbf{r}|)=\frac{(2Z)^{2\gamma+1}r^{2\gamma}}{4\pi r^2\Gamma(2\gamma+1)}\exp^{-2Zr},\quad \gamma=\sqrt{1-Z^2/c^2}. \tag{32}$$

For a finite extension of the nucleus, $r\approx10^{-4}$ a.u., the singularity is removed. Nevertheless, this relativistic singularity problem and the very large contributions of the s components in general (Fig. 2) make a different point charge model from that given in Fig. 1 desirable; in other words the s contributions should be avoided. One can get rid of the spherical contributions if the perturbing charges are placed in three-dimensional space as shown in Fig. 3. The expression (10) for the interaction energy is then written as

$$U_{\mathrm{int}}=\tfrac{1}{2}(2\zeta d^2 q_{zz}-\zeta d^2 q_{xx}-\zeta d^2 q_{yy}), \tag{33}$$

where U_{int} vanishes for spherical contributions.

Since the point charge arrangement of Fig. 3 couples all three EFG components together, the spherical part with $q_{xx}=q_{yy}=q_{zz}$ is annihilated. Numerical inaccuracies in the evaluation of dE/dQ due to large s contributions can therefore be avoided as well. The arrangement of point charges in Fig. 3 is used in all molecular calculations here. In a linear molecule $q_{xx}=q_{yy}$ holds due to rotational symmetry around the z axis and with the validity of the Laplace equation Eq. (33) simplifies to

$$U_{\mathrm{int}}=\tfrac{3}{2}Q q_{zz}. \tag{34}$$

Figure 4 shows the $2p$ contributions to the EFG for atoms up to $Z=85$. Again, the PCNQM model performs well for small displacements d of the charge perturbation. For example, for $d=10^{-4}$ a.u. and $\zeta\in\{+0.2,+0.1,0,-0.1,-0.2\}$ a.u. we obtain for $Z=50$ $q_{zz}=-4166.5$ a.u. in good agreement with the expectation value of -4166.1 a.u. In comparison, $d=10^{-3}$ a.u. yields -4161.8 a.u. Figure 4 also shows different EFG curves for different choices of d. This clearly demonstrates, that the distance d for the point charges should be chosen as small as possible, but large enough to avoid numerical difficulties. $d=10^{-1}$ a.u. is certainly a bad choice, Fig. 4. We also mention that the point charge arrangements shown in Figs. 1 and 3 contain a small hexadecupole contamination of $(4!)^{-1}\zeta d^4$ which can safely be neglected for a small displacement d.

Having discussed different choices of d, we can now analyze how small the charge ζ must be in order to obtain accurate EFGs. Table I shows EFGs for the $2\,^2P$ state of the one-electron atom with $Z=85$. The data clearly show that the

TABLE I. EFGs for one-electron systems (in a.u.). Due to orbital rotations no result could be obtained for some combinations (denoted by $-$).

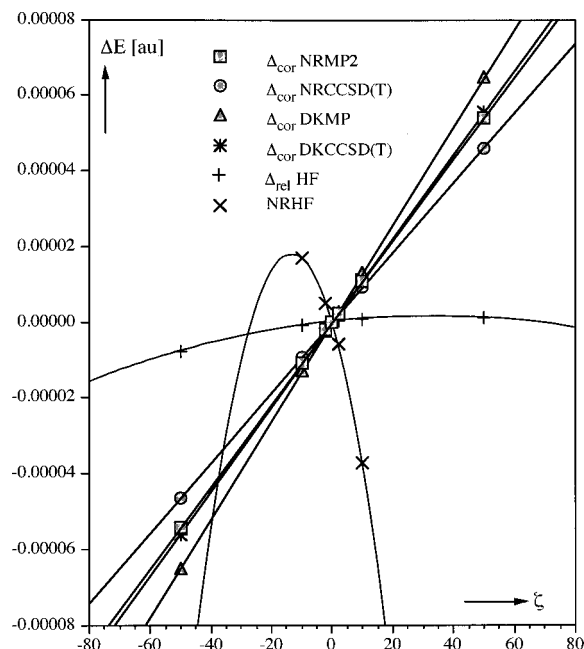| Q	$d=10^{-1}$	$d=10^{-2}$	$d=10^{-3}$	$d=10^{-4}$
10^3	-	-	-	$-20\,469.903$
10^2	-	-	$-20\,403.161$	$-20\,469.903$
10^1	-	-	$-20\,403.167$	$-20\,469.903$
1	1984.112	$-16\,134.180$	$-20\,403.167$	$-20\,469.902$
10^{-1}	1984.113	$-16\,134.184$	$-20\,402.992$	$-20\,468.226$
10^{-2}	1984.113	$-16\,134.184$	$-20\,402.992$	$-20\,468.172$
10^{-3}	1984.113	$-16\,134.184$	$-20\,402.994$	$-20\,469.779$
10^{-4}	1984.113	$-16\,134.183$	$-20\,402.997$	$-20\,489.707$
10^{-5}	1984.113	$-16\,134.182$	$-20\,403.176$	$-20\,690.903$

FIG. 5. The total electronic energies (HF energy, the relativistic and correlation contribution, all set to zero at $\zeta = 0$) for CuF as a function of the applied point charge in the PCNQM model shown in Fig. 3.

EFG is sensitive to the choice of the displacement d, but it is relatively unaffected by the choice of the charge ζ. This can be understood from first order perturbation theory where ζ is linear in the response. As a result, relatively modest to large values of ζ may be used in connection with a small displacement d within the PCNQM model. The (almost) linear behavior of the EFG in ζ (see also the discussion for CuF below) suggests that for the numerical differentiation of Eq. (24) the charge ζ should be chosen as the variable at a fixed displacement d, and not vice versa. Figure 4 also contains the relativistic contribution of the $2p_{3/2}$ EFG, showing that relativistic effects soon become important with increasing nuclear charge Z.

IV. MOLECULAR CALCULATIONS

A. Computational details

All nonrelativistic and scalar relativistic calculations on CuF for the Cu and F EFGs were carried out using the MOLCAS-3 program system[44] at the experimental equilibrium bond distance of $r_e = 3.297\,44$ a.u. We have applied the MOLCAS implementation of Møller–Plesset perturbation theory (MP2),[54] the TITAN algorithm for coupled cluster singles and doubles (CCSD),[55] and the CCSD augmented perturbative correction for the triple excitations (CCSD(T))[56] by Lee, Rice, and Rendell.[57] The implementation of the Douglas–Kroll transformation (DK)[34–36] into the one-electron integral code was done by Hess and modified for the MOLCAS package by Kellö. For the comparison with DK calculations and for estimating spin-orbit effects, fully four-component PCNQM Dirac–Fock (DF) calculations were performed using the program system MOLFDIR.[58] Because of huge disk space and CPU time requirements needed for the DF calculations, a restriction of the basis set was necessary. This medium

TABLE II. Nonrelativistic (NR), Douglas–Kroll (DK) and Dirac–Fock (DF) Cu and F EFGs for CuF with the small basis B1 and the extended basis B2. All values are in a.u.

Method	Cu EFGs basis B1		F EFGs basis B1	
	Contrib.	EFG(el.)	Contrib.	EFG(el.)
	Nonrelativistic			
HF	−1.8039	−1.8039	−0.8515	−0.8515
MP2	+0.6760	−1.1279	+0.3808	−0.4707
CCSD	+0.5994	−1.2045	+0.2885	−0.5630
CCSD(T)	+0.6804	−1.1235	+0.3375	−0.5140
	Douglas–Kroll			
HF	−1.7437	−1.7437	−0.7469	−0.7469
MP2	+0.7901	−1.9536	+0.4205	−0.3264
CCSD	+0.6989	−1.0448	+0.3148	−0.4321
CCSD(T)	+0.8029	−0.9408	+0.3738	−0.3731
	Dirac–Fock			
HF	−1.7562	−1.7562	−0.7712	−0.7712
MP2	+0.7634	−0.9928	+0.4204	−0.3508
CCSD	+0.6867	−1.0695	+0.3165	−0.4547
CCSD(T)	+0.7862	−0.9700	+0.3769	−0.3943
Method	Cu EFGs basis B2		F EFGs basis B2	
	Contrib.	EFG (el.)	Contrib.	EFG(el.)
	Nonrelativistic			
HF	−1.8057	−1.8057	−0.9061	−0.9061
MP2	+0.7485	−1.0572	+0.3964	−0.5097
CCSD	+0.6207	−1.1850	+0.2645	−0.6416
CCSD(T)	+0.7140	−1.0917	+0.3319	−0.5742
	Douglas–Kroll			
HF	−1.7404	−1.7404	−0.7992	−0.7992
MP2	+0.9051	−0.8353	+0.4403	−0.3589
CCSD	+0.7408	−0.9996	+0.2904	−0.5088
CCSD(T)	+0.8642	−0.8762	+0.3702	−0.4290

sized basis set is denoted as B1 in the following. A more flexible basis set for nonrelativistic and DK calculations was subsequently applied (basis set B2). We outline briefly the construction of the two basis sets B1 and B2 listed in Tables III–X. More details are given in the appendix.

1. B1 basis

The starting point for the copper basis is an atomic natural orbital (ANO) basis set created for the first row transition elements by Bauschlicher and Partridge.[59,60] The original $(20s15p10d6f4g) \rightarrow [7s6p4d3f2g]$ general contraction scheme was modified to a $(20s15p11d1f) \rightarrow [10s10p7d1f]$ scheme. We released more primitives in the s, p, and d shell; in particular the p functions have a significant influence on EFGs.[61] A considerable flexibility in the s function set is necessary for a good description of the scalar relativistic effects by the DK formalism.[34–36] For a DK calculation a complete recontraction of the basis set was done using the ANO coefficients of a ROHF calculation.

For fluorine the original aug-cc-pVTZ basis created by Dunning et al.[62,63] was truncated and slightly modified for the four-component calculations. To keep the basis of moderate size the original $(11s6p3d2f) \rightarrow [5s4p3d2f]$ contraction was changed to a $(11s7p1d) \rightarrow [5s4p1d]$ scheme where the eight hardest s and four hardest p exponents were contracted. One hard p exponent of 128.1854 was added for a better description of the spin–orbit coupling of the $2p$

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TABLE III. Copper basis B1 for nonrelativistic calculations.

	Copper Basis B1 nonrelativistic			
s exponents	contraction coefficients			
5430320.90000000	0.856180851(−05)	−0.263319661(−05)	0.984458502(−06)	−0.170861373(−06)
813166.47700000	0.665566476(−04)	−0.204758611(−04)	0.766548449(−05)	−0.132838548(−05)
185054.36000000	0.350046295(−03)	−0.107699934(−03)	0.402434826(−04)	−0.698944372(−05)
52414.65580000	0.147549908(−02)	−0.454735783(−03)	0.170377651(−03)	−0.295053023(−04)
17098.67630000	0.534719068(−02)	−0.165321953(−02)	0.617705789(−03)	−0.107372090(−03)
6172.00200000	0.171435218(−01)	−0.535524536(−02)	0.201118972(−02)	−0.348064054(−03)
2406.44200000	0.490170093(−01)	−0.156631540(−01)	0.587082999(−02)	−0.102197738(−02)
997.41880000	0.121807444(+00)	−0.410957734(−01)	0.155952366(−01)	−0.269873969(−02)
433.77470000	0.248256940(+00)	−0.937565301(−01)	0.358201118(−01)	−0.626184470(−02)
196.32880000	0.356684379(+00)	−0.170912092(+00)	0.680226789(−01)	−0.117989188(−01)
91.10269000	0.283069107(+00)	−0.194850879(+00)	0.805783111(−01)	−0.143563441(−01)
39.23766000	0.704364056(−01)	0.541664143(−01)	−0.228369660(−01)	0.458071224(−02)
19.41507000	−0.738180859(−02)	0.535835895(+00)	−0.333923585(+00)	0.604019958(−01)
9.35944100	0.489349263(−02)	0.480878520(+00)	−0.441736566(+00)	0.882187371(−01)
4.36614000	1.0			
1.95597300	1.0			
0.76459490	1.0			
0.26441920	1.0			
0.08504341	1.0			
0.03384947	1.0			

p exponents	contraction coefficients	
9902.68792000	0.158748287(−03)	0.219867935(−04)
2345.72293000	0.139671036(−02)	0.193474504(−03)
761.35835100	0.780383320(−02)	0.108991642(−02)
290.28189100	0.322296179(−01)	0.455608182(−02)
122.38382600	0.101346442(+00)	0.148038927(−01)
55.17048260	0.231887965(+00)	0.353372864(−01)
25.90214810	0.352467935(+00)	0.574664488(−01)
12.47784790	1.0	
5.91041721	1.0	
2.75576220	1.0	
1.23440823	1.0	
0.50818719	1.0	
0.20300000	1.0	
0.08130000	1.0	
0.03250000	1.0	

d exponents	contraction coefficients
433.77470000	0.252646762(−03)
196.32880000	0.650414760(−03)
91.10269000	0.473407913(−02)
39.23766000	0.180779538(−01)
19.41507000	0.474538032(−01)
9.35944100	1.0
4.36614000	1.0
1.95597300	1.0
0.76459490	1.0
0.26441920	1.0
0.08504341	1.0

f exponent	
1.23440823	1.0

shell.[64] The *d* exponent was modified for the four-component calculations.

In order to create a kinetically balanced four-component wave function and to reduce the size of the small component basis set, the basis set was reoptimized with the restriction that the $d-(f-)$ exponents are a subset of the $s-(p-)$ exponents. The B1 set of exponents and contraction coeffi-

cients is listed in Tables VII–X. The corresponding contraction coefficients for the nonrelativistic and DK calculations were determined by a ROHF calculation of the fully uncontracted set for the copper and fluorine atom where only the coefficients of the occupied orbitals were included in the general contraction scheme. For the DK calculations a different contraction was required especially for the accurate
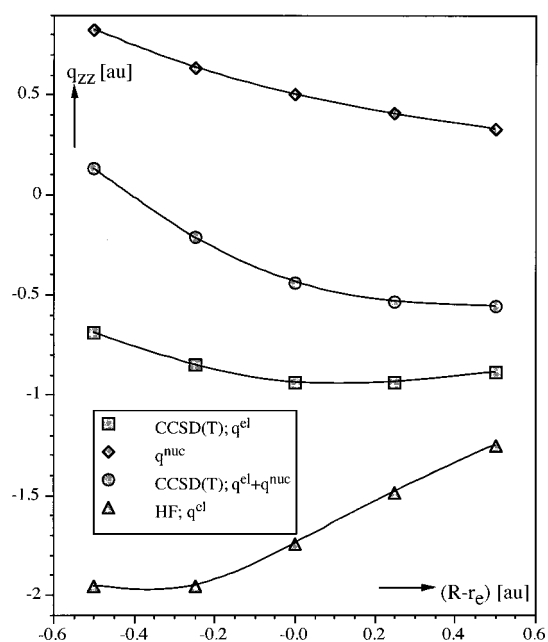
FIG. 6. The EFG as a function of the intermolecular distance R.

description of the innermost s basis functions (see Table IV). Relativistic effects on the fluorine basis set were neglected and a modified augmented correlation consistent pVTZ basis set of Dunning[62] was used.

The small component $(SS|SS)$ integrals in the DF Coulomb calculations consume usually more than 2/3 of the two-electron integrals. A test calculation revealed that leaving out these integrals lowered the total electronic energy by only 7 mH. We therefore neglected such matrix elements. Any errors introduced should be smaller than basis set or correlation errors. Furthermore, neglect of the $(SS|SS)$ integrals will have the greatest affect on the $1s_{1/2}$ orbital, an orbital which has a relatively small indirect contribution to the EFG at the nucleus. The Cu and F primitive basis sets were contracted following the atomic balance scheme.[65] The contracted function representing the inner tail of the $3p_{1/2}$ orbital (both large and small components) of Cu was found to be linearly dependent and was therefore removed. A further contracted function was added to the small component s space for F. The final basis was $L(20s15p11d1f) \rightarrow [10s11p8d1f]$ and $S(15s20p15d11f1g) \rightarrow [9s12p11d8f1g]$ for Cu and $L(11s7p1d) \rightarrow [5s5p1d]$ and $S(7s11p7d1f) \rightarrow [5s5p5d1f]$ for F. The contraction coefficients for this basis is given in Tables VII–X. The finite extension of the Cu and F nuclei were represented by Gaussian functions with exponents 2.767×10^{10} and 5.355×10^{10} for Cu and F, respectively. It should be noted that these finite nuclear extensions are spherically symmetric and have no effect on the EFG at either nucleus. Indeed, the nuclear–nuclear interaction is treated as though each nucleus is a point charge in the MOLFDIR program. It was necessary to assign a finite extension to any point charges added to create the artificial NQM. The exponents of the Gaussians in question were chosen to be 1×10^{20} and therefore all added charges were effectively point charges. The integral cut-offs

for the $(LL|LL)$ and $(LL|SS)$ matrix elements were 10^{-10} and 10^{-8} a.u., respectively. All DF calculations were carried out under C_{4v} symmetry except for the atomic calculations where O_h symmetry was used.

2. B2 basis

The set of copper exponents for the extended nonrelativistic and DK calculations was taken identically from Bauschlicher[59] without further optimization. For the nonrelativistic calculations the following changes concerning the general contraction scheme were made: We removed four in each of the s, p, and d primitives from the contractions and added them as separate basis functions. The g functions given by Bauschlicher[59] were omitted. Furthermore virtual orbitals were not included into the general contraction scheme. This results in a $(20s15p10d6f) \rightarrow [11s10p8d3f]$ contraction (see Tables V and VI).

For fluorine the original set of exponents[62,63] was kept unaltered and no truncations were made. We only released the three softest s and p exponents from the general contraction scheme where the diffuse functions remained uncontracted as in the original set. These modifications changed the original contraction scheme to $(11s6p3d2f) \rightarrow [6s5p3d2f]$.

3. Treatment of electron correlation

For the very expensive DF calculations with basis B1 we had to confine ourselves to a relatively small active orbital space. For the HF, DK, and DF MP2 and CCSD(T) calculations the $1s$, $2s$, $2p$, $3s$, and $3p$ electrons on Cu and the $1s$ electrons on F were frozen. Furthermore, all virtual orbitals with energy greater than 10 a.u. were deleted. For the more accurate nonrelativistic and relativistic DK calculations with basis B2, the active space was extended in such a way that only the $1s$, $2s$, and $2p$ orbitals on Cu and the $1s$ orbital on F were kept frozen.

For the numerical differentiation to obtain q_{zz}, five points with $Q=0.0$, $Q=\pm10^{-6}$, $Q=\pm2.0\times10^{-6}$ a.u. with a displacement of $d=10^{-3}$ a.u. were used. As can be seen in Fig. 5 the charges should not be too large and for the numerical stability of the SCF wave function the distances from the nucleus had to be enlarged accordingly. The SCF convergence applied was below 10^{-12} a.u. In all cases, the nonrelativistic HF EFG expectation value was in very good agreement with the numerical fit. It turned out that one cannot achieve so easily the same numerical stability for the correlated calculations as for the HF results. Therefore, a separate investigation of the influence of electron correlation effects on the EFG was performed, which we discuss in the following.

In Fig. 5 the correlation energy at the MP2 and CCSD(T) level is plotted against the perturbational charge ζ for a wide range of values. For comparison, the energies plotted in Fig. 5 are all set to zero at the charge $\zeta=0$ a.u. Even for high charges ζ, no detectable deviation from a linear behavior can be observed for both the relativistic DK and the nonrelativistic case. This allows for a separate treatment of the electron correlation contribution. The EFG is

$$F^{\alpha\beta} = F_{\text{HF}}^{\alpha\beta} + F_{\text{cor}}^{\alpha\beta}, \tag{35}$$

TABLE IV. Copper basis B1 for Douglas–Kroll calculations.

Copper Basis B1 for DK calculations			
s exponents	contraction coefficients		
5430320.90000000	0.172767635(−03)	−0.541744491(−04)	0.203342038(−04)	0.359687138(−05)
813166.47700000	0.495262499(−03)	−0.155484354(−03)	0.583788938(−04)	0.103249238(−04)
185054.36000000	0.134580109(−02)	−0.423207295(−03)	0.158861225(−03)	0.281097226(−04)
52414.65580000	0.341798156(−02)	−0.107910385(−02)	0.405649742(−03)	0.717111003(−04)
17098.67630000	0.867324495(−02)	−0.275344998(−02)	0.103395249(−02)	0.183132614(−03)
6172.00200000	0.220915987(−01)	−0.710822243(−02)	0.268103238(−02)	0.473568957(−03)
2406.44200000	0.554774820(−01)	−0.182694637(−01)	0.688329906(−02)	0.122136701(−02)
997.41880000	0.128606733(+00)	−0.447510210(−01)	0.170655590(−01)	0.301373876(−02)
433.77470000	0.251741819(+00)	−0.976211268(−01)	0.374810470(−01)	0.667945066(−02)
196.32880000	0.352161077(+00)	−0.172409042(+00)	0.689464851(−01)	0.122049665(−01)
91.10269000	0.274069624(+00)	−0.185873520(+00)	0.769156390(−01)	0.139679693(−01)
39.23766000	0.672214949(−01)	0.735809627(−01)	−0.332461641(−01)	−0.655271895(−02)
19.41507000	0.702626675(−02)	0.540669540(+00)	−0.342403680(+00)	−0.634495103(−01)
9.35944100	0.464153703(−02)	0.466062831(+00)	−0.431536041(+00)	−0.878975831(−01)
4.36614000	1.0			
1.95597300	1.0			
0.76459490	1.0			
0.26441920	1.0			
0.08504341	1.0			
0.03384947	1.0			

p exponents	contraction coefficients	
9902.68792000	0.390076375(−03)	−0.144490257(−03)
2345.72293000	0.204121049(−02)	−0.757187384(−03)
761.35835100	0.971480159(−02)	−0.363308485(−02)
290.28189100	0.372639182(−01)	−0.141038651(−01)
122.38382600	0.113369933(+00)	−0.443121278(−01)
55.17048260	0.254344929(+00)	−0.103533171(+00)
25.90214810	0.382123190(+00)	−0.166127823(+00)
12.47784790	1.0	
5.91041721	1.0	
2.75576220	1.0	
1.23440823	1.0	
0.50818719	1.0	
0.20300000	1.0	
0.08130000	1.0	
0.03250000	1.0	

d exponents	contraction coefficients
433.77470000	−0.361981241(−03)
196.32880000	−0.871101102(−03)
91.10269000	−0.622819857(−02)
39.23766000	−0.233766281(−01)
19.41507000	−0.610575311(−01)
9.35944100	1.0
4.36614000	1.0
1.95597300	1.0
0.76459490	1.0
0.26441920	1.0
0.08504341	1.0

f exponents	
1.23440823	1.0

where $F_{HF}^{\alpha\beta}$ and $F_{cor}^{\alpha\beta}$ are the HF and electron correlation contribution, respectively. Using Eq. (17) it follows that

$$\langle\Psi(Q)|q_{zz}|\Psi(Q)\rangle_0 = \left.\frac{dE_{HF}(Q)}{dQ}\right|_0 + \frac{1}{2Q}\left(E_{cor}(+Q)\right.$$
$$\left. - E_{cor}(-Q)\right). \tag{36}$$

The correlation contributions to the EFGs listed in Tables II and III are therefore determined by adding $1/(2Q) \times \{E_{cor}(+Q) - E_{cor}(-Q)\}$ to the uncorrelated HF, DF, or DK value.

Figure 5 also shows the nonrelativistic HF energies and the relativistic change at the HF level dependent on the point charge ζ. The tangents at $Q = \zeta d^2 = 0$ give the electric field

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TABLE V. Copper basis B2 for nonrelativistic calculations.

Copper Basis B2 for nonrelativistic calculations				
s exponents	contraction coefficients			
5430320.90000000	0.00000900	0.00000300	0.00000100	0.00000000
813166.47700000	0.00006700	0.00002000	0.00000800	0.00000200
185054.36000000	0.00035000	0.00010800	0.00004000	0.00000900
52414.65580000	0.00147600	0.00045500	0.00017000	0.00003700
17098.67630000	0.00534600	0.00165300	0.00062000	0.00013400
6171.99427000	0.01714900	0.00535400	0.00201100	0.00043600
2406.48073000	0.04899800	0.01566800	0.00589300	0.00127600
997.25842700	0.12190100	0.04109100	0.01558700	0.00338400
433.92893000	0.24776500	0.09369200	0.03595300	0.00780200
196.28691500	0.35820700	0.17116500	0.06798500	0.01485700
91.04279780	0.27960800	0.19489100	0.08131600	0.01778800
41.38425100	0.06856800	−0.04407300	−0.01945600	−0.00410300
19.93277820	−0.00122900	−0.52177300	−0.31847800	−0.07396000
9.58189137	1.0			
4.23451601	1.0			
1.98581402	1.0			
0.86708271	1.0			
0.18133919	1.0			
0.08365697	1.0			
0.03626668	1.0			
p exponents	contraction coefficients			
9902.68792000	0.00017200	0.00006400		
2345.72293000	0.00151700	0.00056200		
761.35835100	0.00847700	0.00316400		
290.28189100	0.03501000	0.01322400		
122.38382600	0.11008700	0.04297900		
55.17048260	0.25188500	0.10256800		
25.90214810	0.38291200	0.16690300		
12.47784790	1.0			
5.91041721	1.0			
2.75576220	1.0			
1.23440823	1.0			
0.50818719	1.0			
0.20300000	1.0			
0.08130000	1.0			
0.03250000	1.0			
d exponents	contraction coefficients			
281.09820000	−0.00099000			
84.19382800	−0.00852300			
32.17397800	−0.03903900			
13.63206800	1.0			
6.13197020	1.0			
2.78015440	1.0			
1.22660420	1.0			
0.51470350	1.0			
0.19595350	1.0			
0.07800000	1.0			
f exponents	contraction coefficients			
24.70500000	−0.01405600	−0.02567200	−0.03330600	
9.88210000	−0.08716300	−0.20655300	−0.42748900	
3.95280000	−0.32516600	−0.54633600	−0.41023300	
1.58110000	−0.47882900	−0.04999400	0.87253600	
0.63250000	−0.31614100	0.54621800	−0.07102000	
0.25300000	−0.10227400	0.33082300	−0.65685500	

gradient contributions. Thus we see a small positive contribution from relativity and a large positive contribution from electron correlation compared to the large negative value at the HF level. We also see a nonlinear behavior at the HF level as well as for the relativistic contribution. This demonstrates that small charges ζ together with small distances for the PCNQM model have to be chosen at the HF level in contrast to the electron correlation contribution.

TABLE VI. Copper basis B2 for Douglas–Kroll calculations.

Copper Basis B2 for DK calculations			
s exponents	contraction coefficients		
5430320.90000000	0.172766703(−03)	−0.541753548(−04)	0.203349137(−04)	−0.360070486(−05)
813166.47700000	0.495271061(−03)	−0.155476331(−03)	0.583710167(−04)	−0.103334042(−04)
185054.36000000	0.134574211(−02)	−0.423256147(−03)	0.158908947(−03)	−0.281500924(−04)
52414.65580000	0.341829646(−02)	−0.107887319(−02)	0.405402111(−03)	−0.717247748(−04)
17098.67630000	0.867184459(−02)	−0.275439873(−02)	0.103500913(−02)	−0.183560669(−03)
6171.99427000	0.220967789(−01)	−0.710465137(−02)	0.267691611(−02)	−0.473145619(−03)
2406.48073000	0.554612978(−01)	−0.182823379(−01)	0.689784076(−02)	−0.122566948(−02)
997.25842700	0.128694784(+00)	−0.447222923(−01)	0.170233564(−01)	−0.300804792(−02)
433.92893000	0.251266598(+00)	−0.976252238(−01)	0.375739843(−01)	−0.670582318(−02)
196.28691500	0.353635398(+00)	−0.172462474(+00)	0.687259115(−01)	−0.121700680(−01)
91.04279780	0.270752147(+00)	−0.186577904(+00)	0.777599341(−01)	−0.141585786(−01)
41.38425100	0.654370810(−01)	0.624938352(−01)	−0.289955553(−01)	0.578244063(−02)
19.93277820	−0.116000588(−02)	0.528970016(+00)	−0.327950112(+00)	0.607246780(−01)
9.58189137	1.0		
4.23451601	1.0		
1.98581402	1.0		
0.86708271	1.0		
0.18133919	1.0		
0.08365697	1.0		
0.03626668	1.0		

p exponents	contraction coefficients	
9902.68792000	0.390076328(−03)	0.144488308(−03)
2345.72293000	0.204121268(−02)	0.757209963(−03)
761.35835100	0.971479820(−02)	0.363298297(−02)
290.28189100	0.372639448(−01)	0.141043953(−01)
122.38382600	0.113369968(+00)	0.443105097(−01)
55.17048260	0.254344940(+00)	0.103538881(+00)
25.90214810	0.382123913(+00)	0.166114188(+00)
12.47784790	1.0	
5.91041721	1.0	
2.75576220	1.0	
1.23440823	1.0	
0.50818719	1.0	
0.20300000	1.0	
0.08130000	1.0	
0.03250000	1.0	

d exponents	contraction coefficients
281.09820000	0.102887440(−02)
84.19382800	0.842119515(−02)
32.17397800	0.379737904(−01)
13.63206800	1.0
6.13197020	1.0
2.78015440	1.0
1.22660420	1.0
0.51470350	1.0
0.19595350	1.0
0.07800000	1.0

f exponents	contraction coefficients		
24.70500000	−0.01405600	−0.02567200	−0.03330600
9.88210000	−0.08716300	−0.20655300	−0.42748900
3.95280000	−0.32516600	−0.54633600	−0.41023300
1.58110000	−0.47882900	−0.04999400	0.87253600
0.63250000	−0.31614100	0.54621800	−0.07102000
0.25300000	−0.10227400	0.33082300	−0.65685500

B. Results and discussion

The results of our molecular calculations are summarized in Table II. Relativistic effects are relatively small compared to the large contributions from electron correla-

tion, but both effects lower the absolute value of the EFG. Relativistic effects change the Cu EFG by 0.065 a.u. at the HF level and by 0.216 a.u. at the CCSD(T) level using the B2 DK results. This is nevertheless a 20% change in the

TABLE VII. Copper basis B1 for DF calculations. Large component.

Copper Basis B1 for DF calculations, Large Component			
s exponents	contraction coefficients		
5430320.90000000	0.409300000(−04)	−0.128600000(−04)	0.483000000(−05)	0.850000000(−06)
813166.47700000	0.160180000(−03)	−0.505100000(−04)	0.189800000(−04)	0.336000000(−05)
185054.36000000	0.594580000(−03)	−0.187880000(−03)	0.705400000(−04)	0.124900000(−04)
52414.65580000	0.203033000(−02)	−0.643900000(−03)	0.242280000(−03)	0.428300000(−04)
17098.67630000	0.651327000(−02)	−0.207331000(−02)	0.778530000(−03)	0.138000000(−03)
6172.00200000	0.193403700(−01)	−0.622698000(−02)	0.234930000(−02)	0.415020000(−03)
2406.44200000	0.525894000(−01)	−0.173007500(−01)	0.651677000(−02)	0.115688000(−02)
997.41880000	0.126158240(+00)	−0.438152200(−01)	0.167052500(−01)	0.295091000(−02)
433.77470000	0.250416320(+00)	−0.969048900(−01)	0.371954000(−01)	0.663089000(−02)
196.32880000	0.352286800(+00)	−0.172124080(+00)	0.688125300(−01)	0.121851700(−01)
91.10269000	0.274667780(+00)	−0.186157110(+00)	0.770214300(−01)	0.139916300(−01)
39.23766000	0.673434400(−01)	0.732995600(−01)	−0.331125300(−01)	−0.653091000(−02)
19.41507000	−0.704650000(−02)	0.540694160(+00)	−0.342378430(+00)	−0.634663500(−01)
9.35944100	0.465008000(−02)	0.465927980(+00)	−0.431468360(+00)	−0.879215700(−01)
4.36614000	1.0			
1.95597300	1.0			
0.76459490	1.0			
0.26441920	1.0			
0.08504341	1.0			
0.03384947	1.0			

p exponents	contraction coefficients		
9902.68792000	0.586490000(−03)	0.200890000(−03)	−0.744600000(−04)
2345.72293000	0.234243000(−02)	0.163737000(−02)	−0.607260000(−03)
761.35835100	0.105574000(−01)	0.883796000(−02)	−0.330320000(−02)
290.28189100	0.389038100(−01)	0.357712900(−01)	−0.135327100(−01)
122.38382600	0.116470520(+00)	0.111065650(+00)	−0.133700300(−01)
55.17048260	0.257631190(+00)	0.252165730(+00)	−0.102597820(+00)
25.90214810	0.382239230(+00)	0.381831510(+00)	−0.165848820(+00)
12.47784790	1.0		
5.91041721	1.0		
2.75576220	1.0		
1.23440823	1.0		
0.50818719	1.0		
0.20300000	1.0		
0.08130000	1.0		
0.03250000	1.0		

d exponents	contraction coefficients	
433.77470000	−0.238730000(−03)	−0.257190000(−03)
196.32880000	−0.560390000(−03)	−0.653830000(−03)
91.10269000	−0.400627000(−02)	−0.471897000(−02)
39.23766000	−0.149480100(−01)	−0.179077200(−01)
19.41507000	−0.389506600(−01)	−0.469343900(−01)
9.35944100	1.0	
4.36614000	1.0	
1.95597300	1.0	
0.76459490	1.0	
0.26441920	1.0	
0.08504341	1.0	

f exponents	
1.23440823	1.0

EFG due to relativity! The relativistic change using the mass-velocity and Darwin term at the HF level estimated earlier for CuF (0.13 a.u.)[61] is therefore overestimated showing the limitation of the MVD method. Comparing DK with DF, the deviation between both results (0.03 a.u. at the CCSD(T) level) should be due to the slightly different basis sets applied and the difference between both relativistic operators, which should mainly be the spin–orbit coupling operator.

In order to study the effects of electron correlation on the EFG more detailed, we chose different active orbital spaces according to the different shells of copper and fluorine. As

TABLE VIII. Copper basis B1 for DF calculations. Small component.

Cu Basis B1 for DF calculations, Small component			
s exponents	contraction coefficients		
9902.68792000	0.293430000(−03)		
2345.72293000	0.110319000(−02)		
761.35835100	0.328364000(−02)		
290.28189100	0.804790000(−02)		
122.38382600	0.159775800(−01)		
55.17048260	0.239997500(−01)		
25.90214810	0.244729200(−01)		
12.47784790	1.0		
5.91041721	1.0		
2.75576220	1.0		
1.23440823	1.0		
0.50818719	1.0		
0.20300000	1.0		
0.08130000	1.0		
0.03250000	1.0		

p exponents	contraction coefficients		
5430320.90000000	0.138730000(−03)	−0.434700000(−04)	0.163100000(−04)	0.289000000(−05)
813166.47700000	0.422090000(−03)	−0.132350000(−03)	0.497200000(−04)	0.879000000(−05)
185054.36000000	0.104184000(−02)	−0.326650000(−03)	0.122490000(−03)	0.217000000(−04)
52414.65580000	0.230401000(−02)	−0.724080000(−03)	0.272210000(−03)	0.481000000(−04)
17098.67630000	0.470076000(−02)	−0.148151000(−02)	0.555540000(−03)	0.984800000(−04)
6172.00200000	0.892988000(−02)	−0.284628000(−02)	0.107266000(−02)	0.189440000(−03)
2406.44200000	0.157178600(−01)	−0.511989000(−02)	0.192611000(−02)	0.341910000(−03)
997.41880000	0.247909400(−01)	−0.852993000(−02)	0.324877000(−02)	0.573770000(−03)
433.77470000	0.328410900(−01)	−0.125993600(−01)	0.483119000(−02)	0.861200000(−03)
196.32880000	0.312914500(−01)	−0.151676200(−01)	0.605872000(−02)	0.107273000(−02)
91.10269000	0.166759600(−01)	−0.112310600(−01)	0.464499000(−02)	0.843750000(−02)
39.23766000	0.268732000(−02)	0.287746000(−02)	−0.129574000(−02)	−0.255700000(−03)
19.41507000	−0.198140000(−03)	0.150573200(−01)	−0.952484000(−02)	−0.176539000(−02)
9.35944100	0.907400000(−04)	0.901526000(−02)	−0.834229000(−02)	−0.169986000(−02)
4.36614000	1.0		
1.95597300	1.0		
0.76459490	1.0		
0.26441920	1.0		
0.08504341	1.0		
0.03384947	1.0		

5430320.90000000	0.0		
813166.47700000	0.0		
185054.36000000	0.0		
52414.65580000	0.0		
17098.67630000	0.0		
6172.00200000	0.0		
2406.44200000	0.0		
997.41880000	0.0		
433.77470000	0.687100000(−04)		
196.32880000	0.117090000(−03)		
91.10269000	0.572730000(−03)		
39.23766000	0.141999000(−02)		
19.41507000	0.261046000(−02)		
9.35944100	0.0		
4.36614000	0.0		
1.95597300	0.0		
0.76459490	0.0		
0.26441920	0.0		
0.08504341	0.0		
0.03384947	0.0		

Cu basis B1 for DF calculations, SC contd.		
d exponents	contraction coefficients	
9902.68792000	0.293430000(−3)	0.917200000(−04)	0.33960000(−04)
2345.72293000	0.110319000(−02)	0.389240000(−03)	0.14418000(−03)
761.35835100	0.328364000(−02)	0.122814000(−02)	0.45851000(−03)
290.28189100	0.804790000(−02)	0.310916000(−02)	0.11749900(−02)

TABLE VIII. (*Continued.*)

d exponents	Cu basis B1 for DF calculations, SC contd. contraction coefficients		
122.38382600	0.159775800(−01)	0.630880000(−02)	0.24612100(−02)
55.17048260	0.239997500(−01)	0.964789000(−02)	0.39222800(−02)
25.90214810	0.244729200(−01)	0.100252600(−01)	0.43515900(−02)
12.47784790	1.0		
5.91041721	1.0		
2.75576220	1.0		
1.23440823	1.0		
0.50818719	1.0		
0.20300000	1.0		
0.08130000	1.0		
0.03250000	1.0		

f exponents	contraction coefficients	
433.77470000	−0.687100000(−04)	−0.524500000(−04)
196.32880000	−0.117090000(−03)	−0.906700000(−04)
91.10269000	−0.572730000(−03)	−0.447560000(−03)
39.23766000	−0.141999000(−02)	0.111808000(−02)
19.41507000	−0.261046000(−02)	−0.206393000(−02)
9²·35944100	1.0	
4.36614000	1.0	
1.95597300	1.0	
0.76459490	1.0	
0.26441920	1.0	
0.08504341	1.0	

g exponents		
1.23440823	1.0	

expected, at the MP2 level the main contribution comes from the $Cu(3d4s)F(2p)$ shell, $+0.714$ a.u. However, the core $Cu(3s3p)F(2s)$ shell contributes significantly to the EFG with $+0.187$ a.u. A very small electron correlation contribution comes from the remaining $Cu(1s2s2p)F(1s)$ core with $+0.003$ a.u.

A comparison of our PCNQM model with the Cu and F EFGs in CuF derived from expectation values over the EFG operator is essential. At the nonrelativistic HF level using basis set B1 we obtain for the electronic part of the EFG -1.8047 a.u. for Cu and -0.8515 a.u. for F. Comparing with the data listed in Table II (-1.8039 a.u. for Cu and -0.8515 a.u. for F) we see that the PCNQM derived EFGs are in excellent agreement. At the DK level, however, we obtain the following SCF expectation values: -1.8311 a.u. for Cu and -0.7452 a.u. for F not in so good agreement with our model (-1.7437 a.u. for Cu and -0.7469 a.u. for F). However, we believe that the difference is due to the error introduced by the use of the DK wave function on the untransformed EFG operator, as has been pointed out recently by Sadlej.[37]

Experimental results from hyperfine interaction in the rotational spectrum of CuF give the following nuclear quadrupole coupling constants (NQCC): 21.95(10) MHz for [63]Cu and 20.32(10) MHz for [65]Cu.[66] If we use the recommended NQMs for copper, $-220(15)$ mb for [63]Cu and $-204(14)$ mb for [65]Cu,[6] and the well known formula for converting EFGs in a.u. to coupling constants in MHz,

$$e^2qQ/h \text{ [Mhz]} = 234.9 eq \text{ [a.u.]} eQ \text{ [b]} \qquad (37)$$

we obtain the following NQCCs at the relativistic CCSD(T) level for [63]Cu (values for [65]Cu are set in parentheses): DK 22.7 (21.0) MHz, DF 24.2 (22.4) MHz with basis set B1, and DK 19.3 (17.9) with basis set B2. We used the nuclear component of the EFG as shown in Eq. (3) which yields $+0.502\,04$ a.u. at the experimental CuF bond distance of $r_e = 3.297\,44$ a.u. If we take the DF value which contains spin–orbit coupling and correct for the basis set incompleteness by using the DK difference between both basis sets, we obtain the final corrected NQCCs of 20.8 MHz for [63]Cu and 19.3 MHz for [65]Cu. This is roughly 1 MHz below the experimental values but within the accuracy of the published NQM.

In order to estimate errors from basis set incompleteness and restrictions in the active orbital space we performed two coupled cluster calculations with charge $\zeta = \pm 2$ a.u. These calculations were very expensive in computer time and disk space requirements and reached the limit of our capacity. The basis set on Cu was the B2 basis set extended by the Bauschlicher set of four g-functions contracted to two. In this case we obtain the following EFGs for copper (in a.u.): DK -1.7407, DK$+$MP2 -0.8587, DK$+$CCSD -1.0595, DK$+$CCSD(T) -0.9160. A comparison with Table II shows that the uncorrelated DK value is virtually unchanged compared to the basis set without g functions. If we take the CCSD(T) value plus nuclear contribution of -0.4140 a.u. and correct for spin–orbit coupling as described above, we obtain the corrected NQCCs of 22.9 MHz for [63]Cu and 21.2 MHz for [65]Cu. We note that the triples correction in the

TABLE IX. Fluorine basis B1 for DF calculations. Large component.

Fluorine Basis B1 DF, Large Component		
s exponents	contraction coefficients	
19500.00000000	0.542000000(−03)	−0.126000000(−03)
2923.00000000	0.402500000(−02)	−0.938000000(−03)
664.50000000	0.204550000(−01)	−0.478900000(−02)
187.50000000	0.794650000(−01)	−0.192480000(−01)
60.62000000	0.230879000(+00)	−0.598860000(−01)
21.42000000	0.432570000(+00)	−0.140253000(+00)
7.95000000	0.349022000(+00)	−0.176072000(+00)
2.25700000	0.430370000(−01)	0.173085000(+00)
0.88150000	1.0	
0.30410000	1.0	
0.09150000	1.0	
p exponents	contraction coefficients	
128.18540000	0.151700000(−02)	0.14390000(−02)
43.88000000	0.152230000(−01)	0.15087000(−01)
9.92600000	0.106235000(+00)	0.10567500(+00)
2.93000000	0.316786000(+00)	0.31608800(+00)
0.91320000	1.0	
0.26720000	1.0	
0.07361000	1.0	
d exponent		
0.88150000	1.0	

TABLE X. Fluorine basis B1 for DF calculations. Small component.

Fluorine Basis B1 DF, Small Component		
s exponents	contraction coefficients	
128.18540000	0.221000000(−03)	0.84000000(−04)
43.88000000	0.123800000(−02)	0.51500000(−03)
9.92600000	0.421900000(−02)	0.17170000(−02)
2.93000000	0.684300000(−02)	0.27920000(−02)
0.91320000	1.0	
0.26720000	1.0	
0.07361000	1.0	
p exponents	contraction coefficients	
19500.00000000	0.451000000(−03)	−0.105000000(−03)
2923.00000000	0.134900000(−02)	−0.314000000(−03)
664.50000000	0.330600000(−02)	−0.773000000(−03)
187.50000000	0.685600000(−02)	−0.165900000(−02)
60.62000000	0.113510000(−01)	−0.294200000(−02)
21.42000000	0.126540000(−01)	−0.410000000(−02)
7.95000000	0.622300000(−02)	−0.313700000(−02)
2.25700000	0.409000000(−03)	0.164300000(−02)
0.88150000	1.0	
0.30410000	1.0	
0.09150000	1.0	
d exponents	contraction coefficients	
128.18540000	0.122000000(−03)	0.10200000(−03)
43.88000000	0.803000000(−03)	0.63100000(−03)
9.92600000	0.271900000(−02)	0.21030000(−02)
2.93000000	0.441600000(−02)	0.34190000(−02)
0.91320000	1.0	
0.26720000	1.0	
0.07361000	1.0	
f exponent		
0.88150000	1.0	

coupled cluster procedure is quite large and one would have to go beyond CCSD(T) in order to accurately determine the NQM for Cu. Nevertheless, our results lend strong support for the NQM of 0.22 b.[6]

Another source of error is the neglect of vibrational/rotational corrections to the EFG which can be quite substantial. Basis set B2 yields the following spectroscopic constants for CuF at the DK level obtained from a five point polynomial fit (experimental values are set in parentheses[67]): $r_e = 175.0$ pm (174.5 pm), $\omega_e = 610$ cm^{-1} (623 cm^{-1}). Previously obtained correlated results on CuF by other authors give longer bond distances, i.e., 179.6 pm,[61] 178 pm[68] or 176.7 pm[69] at the CI or coupled-cluster level. The EFG curves are shown in Fig. 6. For further analysis we shifted our DK potential curve to the experimental minimum, determined numerically the vibrational-rotational wave functions and evaluated the vibrational-rotational averaged EFG. The correction to the vibrational-rotational ground state is small, i.e., $\langle q^{\mathrm{el}} \rangle = -0.9377$ a.u. compared to -0.9412 a.u. at the minimum bond distance r_e, and $\langle q^{\mathrm{nuc}} \rangle = +0.4986$ a.u. compared to $+0.5020$ a.u. at r_e. Hence the total field gradient $\langle q \rangle = -0.4391$ a.u. is almost identical to $q = -0.4392$ a.u. at r_e because nuclear and electronic corrections cancel out. Furthermore, Fig. 6 shows that the total EFG(R) curve exhibits only a small slope and curvature around r_e.

We also applied a point charge model in order to obtain the CuF dipole moment[70] which is 6.29 D at the uncorrelated DK level and 5.44 D at the DK CCSD(T) level using basis set B1. Nearly the same value of 5.43 D was also obtained using a MP2 correlation treatment instead of the CCSD(T). This is not in so good agreement with the experimental value of 5.77(20) D.[66] Spin–orbit effects are also negligible as DF calculations show (6.29 D at the DF level and 5.43 D at the

DF/MP2 and DF/CCSD(T) level). We repeated the calculations with the large basis set B2. The final dipole moments are 6.13 D at the uncorrelated DK level and 5.30 D at the DK CCSD(T) level. Thus increasing the quality of the basis set lowers the dipole moment. Hence, either the correlation procedure and basis sets applied are not accurate enough, or the experimental dipole moment is too large.

We like to mention that it is trivial to implement the PCNQM model into any *ab-initio* or density functional program. With the point charge arrangement shown in Fig. 3 one can determine the complete EFG tensors for an unsymmetric molecule. The PCNQM model can also be easily applied to the solid state. Work in this direction is underway. However, we recommend strongly that integral accuracies and SCF convergence is set to a very tight criterion before the PCNQM model is applied. Finally, we note that in the nonrelativistic case the analytical evaluation of EFGs is superior. However, fully relativistic four-component calculations for large molecules at the correlated level are currently not feasible. In this case the PCNQM model combined with any scalar or two-component relativistic method is an attractive alternative.

ACKNOWLEDGMENTS

APPENDIX

Tables III–X[12] list all basis sets used for copper and the DF basis set for fluorine. The original exponents for the copper basis set were taken from Bauschlicher and Partridge[59,60] and modified for the relativistic calculations as described in the text. The unmodified Dunning fluorine basis sets was obtained from the Extensible Computational Chemistry Environment Basis Set Database.[62,63,71] The total electronic energies at the SCF level are as follows (in a.u.): for copper $-1638.961\,969$ (HF), $-1653.120\,998$ (DK), $-1653.451\,738$ (DF); for fluorine $-99.402\,879$ (HF), $-99.483\,257$ (DK), $-99.494\,413$ (DF) using basis B1. For basis B2 we obtain for copper $-1638.962\,924$ (HF), $-1653.121\,578$ (DK); for fluorine $-99.402\,100$ (HF), $-99.483\,191$ (DK). The HF limit is estimated from numerical calculations: $-1638.963\,742$ for copper and $-99.409\,871$ for fluorine at the HF level, and $-1653.455\,269$ for copper and $-99.502\,298$ for fluorine at the DF level.[72,73] For both the atomic numerical and algebraic DF calculations a Gauss-type charge distribution for the nuclear extension was used, and the $(SS|SS)$ integrals were included.

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[70] Two opposite point charges with $\zeta=0$, ± 1, ± 2, ± 3 and ± 4 a.u. at a distance of ± 1000 a.u. from the center of mass in CuF were chosen. This gives an accuracy of at least two digits after the decimal point.

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