

Note: Counterintuitive gauge-dependence of nuclear magnetic resonance shieldings for rare-gas dimers: Does a natural gauge-origin for spherical atoms exist?

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Nowadays calculations of nuclear magnetic resonance (NMR) shieldings are usually performed using special techniques [mostly gauge including atomic orbitals (GIAO) but also individual gauge for localized orbitals (IGLO) and others] to overcome the so-called gauge-origin problem: dependence of the results, obtained with the finite bases, on the gauge origin of the vector potential due to an external magnetic field. It is still surprising how much can sometimes be learned from “outdated” calculations of NMR shieldings with a common gauge origin (CGO). This is especially true when calculations lead to counterintuitive results as in the case of fully relativistic calculations of NMR shieldings in a xenon dimer (with $R_{\text{Xe-Xe}} = 20 \text{ \AA}$).¹ In particular, the shift relative to an isolated Xe atom was larger for the Xe placed at the CGO position than for the other nucleus (for which GIAO shieldings were equal to that of an isolated Xe atom). This finding contradicts the intuitive expectation that better results should be obtained for the nucleus at the CGO position.² Since we have verified that this surprising gauge-dependence of the relativistic results is very similar in nonrelativistic calculations (regardless of the large difference in the absolute shieldings), below we will analyze this observation in detail using a more convenient nonrelativistic approach.³

The nonrelativistic results for the calculated Xe shieldings for the isolated Xe and xenon dimer are presented in Table I. The CGO was chosen at the position of the first xenon atom. The Xe–Xe distance in xenon dimer was taken to be 10, 20, and 200 Å to show the distance dependence of the effect. Despite the small values, the deviation from the shielding of the isolated Xe atom is clearly larger for the first nucleus (placed at the CGO position). The same trend was also found for other rare-gas dimers. For the nucleus at the CGO position shift with respect to an isolated atom turns out to be inversely proportional to the distance to the other atom, giving spuriously large shifts at shorter distances. For the shift at the other atom the values are all very close to the isolated atom value. This dependence displayed in Table I is counterintuitive because one would expect that the best choice for a common gauge position would be on the position of the atom where one wishes to measure the chemical shielding. Where is the catch?

The key point is that despite common belief there is no natural gauge origin for an isolated atom with a spherical

distribution of the electron density. **The NMR shielding of a spherical atom is gauge-origin independent** even for a finite basis set! The same holds for the separate diamagnetic and paramagnetic contributions (the latter is always equal to zero). This contradicts some statements made earlier in literature.⁴ Exactly, this wrong common belief leads us to conceive these results for rare gas dimers as counterintuitive. Below we will prove the above statement and explain the observed gauge-dependence of NMR shieldings for rare-gas dimers.

Let us first consider the gauge dependence separately for the paramagnetic and diamagnetic contributions in the case of an atom with spherically symmetric distribution of the electron density. The usual argument is that, when the gauge for the uniform external magnetic field is chosen at the position of the nucleus of interest, the paramagnetic current vanishes and thus the whole paramagnetic contribution also vanishes. It is then assumed that this is not the case for a different position of the gauge because then the paramagnetic current is nonzero. This argument is, however, incorrect as can be shown by applying Dalgarno’s exchange theorem⁵ and taking the magnetic field due to the nuclear magnetic moment as the primary perturbation. While the magnetic field due to the external magnetic field depends on the gauge origin \mathbf{G} , the vector potential due to the nuclear magnetic moment does not:⁶

$$\mathbf{A}_G = \frac{1}{2} \mathbf{B} \times \mathbf{r}_G, \quad \mathbf{A}_N = \frac{\mathbf{m} \times \mathbf{r}_N}{r_N^3}. \quad (1)$$

With the “natural gauge” (N) for \mathbf{A}_N the paramagnetic current vanishes for a spherical atom even in the case of a finite basis set. As a result there is never a paramagnetic current to interact with the external magnetic field and the paramagnetic contribution to the shielding of a spherical atom is gauge independent and equal to zero. Since the sum of diamagnetic and paramagnetic contributions must be gauge invariant in the limit of infinite basis set, one can already deduce that the diamagnetic contribution should also be gauge origin independent for spherical atoms. However, one can also prove this directly.

The usual nonrelativistic diamagnetic operator

$$h_{vu}^{\text{dia}} = \frac{\delta_{uv} \mathbf{r}_G \cdot \mathbf{r}_N - r_{G,u} r_{N,v}}{r_N^3}. \quad (2)$$

TABLE I. Isotropic shieldings (in ppm) on ^{129}Xe . Shifts with respect to the isolated atom are given in parentheses. The common gauge origin has been chosen on the first Xe atom.

System	R (Å)	Method	First atom	Second atom
Xe		CGO	5642.18	
Xe ₂	20	GIAO	5642.18	5642.18
Xe ₂	10	CGO	5669.24 (-27.06)	5642.18 (0.00)
Xe ₂	20	CGO	5655.71 (-13.53)	5642.18 (0.00)
Xe ₂	200	CGO	5643.53 (-1.35)	5642.18 (0.00)

can be rewritten in the following form:

$$h_{vu}^{\text{dia}} = \frac{\delta_{vu} r_N^2 - r_{N,u} r_{N,v}}{r_N^3} - \frac{\delta_{vu} (\mathbf{G} - \mathbf{N}) \cdot \mathbf{r}_N - (\mathbf{G} - \mathbf{N})_u r_{N,v}}{r_N^3}. \quad (3)$$

The first term in Eq. (3) is gauge independent since the operator does not refer to the gauge origin \mathbf{G} . For the second term we should consider the location of the electron density that contributes to the shielding. We take the expectation value

$$\begin{aligned} \langle h_{vu}^{\text{dia}} \rangle &= \int \rho_M(\mathbf{r}) h_{vu}^{\text{dia}} dV = \delta_{vu} \left(\int \frac{\rho_M(\mathbf{r})}{r_N} dV - (\mathbf{G} - \mathbf{N}) \right. \\ &\quad \cdot \left. \int \frac{\rho_M(\mathbf{r}) \mathbf{r}_N}{r_N^3} dV \right) - \left(\int \frac{\rho_M(\mathbf{r}) r_{N,u} r_{N,v}}{r_N^3} dV \right. \\ &\quad \left. - (G - N)_u \int \frac{\rho_M(\mathbf{r}) r_{N,v}}{r_N^3} dV \right), \quad (4) \end{aligned}$$

where we define \mathbf{M} as the center of the spherically symmetric charge distribution. If \mathbf{M} coincides with the position of the nucleus \mathbf{N} ($\mathbf{M} = \mathbf{N}$; in other words if we want to measure the “own atom” contribution to the shielding), the gauge-origin dependent terms disappear because of the odd parity of the integrands. This proves that for a single spherical atom the shielding is gauge-origin independent.

Let us now consider the dependence of the diamagnetic term on the gauge for two noninteracting spherical atoms for which the formulas derived above can also be used. At distances as large as 20 Å a direct overlap of atomic orbitals from different atoms should be negligible, and we should be able to separate the contributions to the shieldings into two additive contributions from the different atoms. We then define the other atom contribution: the shielding contribution of an atom with an origin \mathbf{M} that does not coincide with \mathbf{N} ($\mathbf{M} \neq \mathbf{N}$). If the atoms are far enough apart, we may make the approximation $\rho_M(\mathbf{r}) \approx N_M \delta(\mathbf{r} - \mathbf{M})$, with N_M being the number of electrons of atom \mathbf{M} , and obtain

$$\frac{1}{3} \sum_v \langle h_{vv}^{\text{dia}} \rangle = \frac{2N_M}{3|\mathbf{M} - \mathbf{N}|} - \frac{2N_M (\mathbf{G} - \mathbf{N}) \cdot (\mathbf{M} - \mathbf{N})}{3|\mathbf{M} - \mathbf{N}|^3}. \quad (5)$$

In this case, the diamagnetic shielding does depend on the gauge origin. If we place the gauge origin at the position of the measurement ($\mathbf{G} = \mathbf{N}$), the last term disappears and an appreciable shielding with an inverse dependence on the distance results. This term should of course be compensated by a paramagnetic contribution of the same magnitude and opposite sign. In order to do so the basis set should, however, be able to represent the first order perturbed wave function

resulting from the effect of an off-center vector potential. In practice this will not be the case, leading to an underestimation of the paramagnetic contribution. This explains the trend seen in the fourth column of Table I. The fifth column of the table corresponds to the case where we place the gauge origin at the center of the charge distribution ($\mathbf{G} = \mathbf{M}$), so that the two terms of Eq. (5) cancel and the diamagnetic other atom contribution to the shielding is zero. With this choice of gauge, the paramagnetic contribution to shielding from a neighboring atom is also zero. We note that use of London orbitals or IGLO will effectively move the gauge origin to the center of the charge density and correspond to this choice of gauge origin on the second atom.

In conclusion, we would like to make three notes. First, the considerations discussed above are also applicable to molecules to some extent. For example, if one chooses the common gauge origin on one of the carbons in C₂H₄ molecule, the calculated isotropic shielding for another carbon (60.4 ppm) is closer to the GIAO value (61.3 ppm) than for the first one (67.5 ppm).⁷ Second, sometimes we are used to apply an intuitive reasoning that may later be proven to be wrong. In such cases, as with the notion that the gauge origin for an external magnetic field is best placed at the position where one wishes to measure the shielding, it is important to correct our vision of the problem. Third, the argument that a spherical atom has a natural gauge at the atom position is a good justification of the IGLO method for calculation of magnetic susceptibilities, but does not directly transfer to NMR nuclear shieldings. IGLO works well for this property for a slightly different reason. The orbital localization procedure will yield a set of roughly spherically symmetric localized MOs, for which we can conclude (based on the considerations presented above) that all contributions from those centered on the nucleus of interest are anyway almost gauge-independent. The only noticeable gauge dependence comes from the “other centers” contribution, for which it is important to place the gauges at the centers of these localized MOs to prevent imperfect cancellation of large diamagnetic and paramagnetic contributions.

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¹ S. Komorovský, M. Repiský, O. L. Malkina, and V. G. Malkin, *J. Chem. Phys.* **132**, 154101 (2010).

² Here we do not consider the ¹H nucleus where the contribution from the neighboring atom to the ¹H shift usually dominates.

³ The Hartree-Fock method and the uncontracted TZ basis (K. G. Dyall, *Theor. Chem. Acc.* **108**, (2002) 335; **109**, (2003) 284) were employed.

⁴ W. Kutzelnigg, U. Fleischer, and M. Schindler, in *NMR Basis Principles and Progress* (Springer, Berlin Heidelberg, 1990), Vol. **23**, p. 165.

⁵ A. Dalgarno and A. L. Stewart, *Proc R. Soc. London, Ser. A* **238**, 269 (1956); **238**, 276 (1956).

⁶ Here \mathbf{N} is the position of the nucleus, \mathbf{m} is the magnetic moment of the nucleus, and \mathbf{r}_Y the position relative to point \mathbf{Y} .

⁷ Hartree-Fock calculations with IGLO-II basis (Ref. 4).