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Computational modeling of isotropic electron paramagnetic resonance spectra of doublet state main group radicals ☆

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Abstract

The combined use of theoretical and mathematical methods in the analysis of electron paramagnetic resonance data has greatly increased the ability to interpret even the most complex spectra reported for doublet state inorganic main group radicals. This personal account summarizes the theoretical basis of such an approach and provides an in-depth discussion of some recent illustrative examples of the utilization of this methodology in practical applications. The emphasis is on displaying the enormous potential embodied within the approach.

Keywords: EPR spectroscopy; Main group radicals; Spectral simulation; DFT calculations

1. Introduction

Isotropic (solution state) electron paramagnetic resonance (EPR) spectra of doublet state organic radicals are usually simple to interpret. There are two main arguments which promote the above statement: from the different nuclei typically present in organic systems, only hydrogen and nitrogen have spin-active isotopes with significant (approx. 100%) natural abundances, and the values of nuclear spin for both ^{1}H and ^{14}N nuclei are low, $I = 1/2$ and 1, respectively [1]. In the majority of cases, this leads to simple and easily detectable splitting patterns in the experimental spectrum [2]. Conversely, isotropic EPR spectra of inorganic main group radicals including other s- and p-block elements than hydrogen and nitrogen are often poorly resolved due to the hyperfine coupling (hfc) of the unpaired electron to magnetically active nuclei with large nuclear spin values ($I > 1$) and more than one naturally abundant spin-active isotope (see Fig. 1) [1].

The complexity in the EPR spectra of main group radicals containing multiple spin-active nuclei generally renders it difficult to extract accurate values of hyperfine coupling (hfc) constants from the experimental spectrum. Since such data are used to gather information of the spin distribution within a paramagnetic molecule, this is quite problematic, as it can impede researchers from gaining a thorough understanding of a particular radical system. In addition, without any knowledge of the hfc constants, it is impossible to produce a simulation of the experimental spectrum which will most likely prevent the identification of the observed radical species. Thus, it is evident that accurate hyperfine parameters play a prominent role in the study of paramagnetic systems.

One possible and very often used method to overcome the above difficulties in spectral interpretation is to employ theoretical first principles methods to calculate

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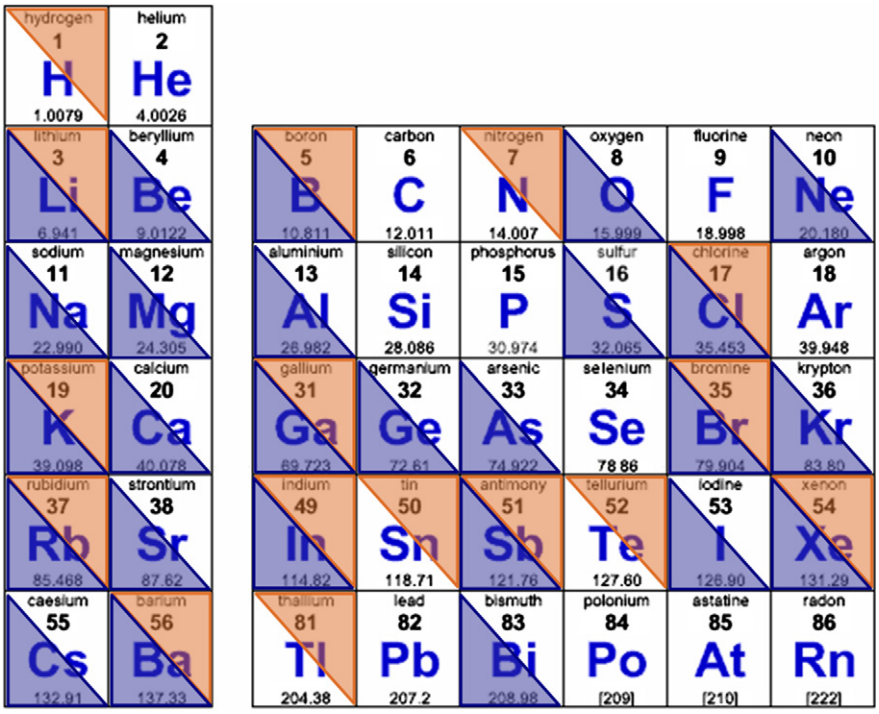

Fig. 1. The 42 different s- and p-block elements. Lower triangle denotes an element for which nuclear spin is greater than one and upper triangle denotes an element with more than one spin-active isotope.

the magnitudes of the hfcs and then compare these results to data extracted from the experimental spectrum [3]. In fact, there is a long history of using theoretical calculations in the interpretation of EPR spectra as perturbation molecular orbital and semi-empirical methods have been used as early as the 50's and 60's [4]. However, an even more powerful approach is to employ the calculated hfc constants as initial estimates of the true spectral parameters and then use iterative least-squares fit based methods to automatically refine the simulation with respect to the experimental EPR spectrum. We have recently shown that this technique can be an extremely successful tool in the assignment and interpretation of complex EPR spectra reported for inorganic main group radicals [5]. This short personal account briefly reviews the theoretical basis of the approach and summarizes the results from its application to the analysis of some paramagnetic systems.

2. Theoretical and computational considerations

2.1. Theoretical methods for calculation of isotropic hyperfine coupling constants

The 3×3 hyperfine coupling tensors $A(i)$ describe the interaction of the unpaired electron with the spin-active nuclei i [6]. They can be separated into isotropic and anisotropic components of which only the former is discussed herein. A good (first-order) approximation of the isotropic hfc $A_{\mathrm{iso}}(i)$ for nucleus i is given by the Fermi contact interaction term

$$A_{\mathrm{iso}}(i) = \frac{8\pi}{3} g_{\mathrm{e}} \beta_{\mathrm{e}} g_i \beta_{\mathrm{n}} \langle \Psi | \delta(r_i) S_Z | \Psi \rangle = \frac{8\pi}{3} g_{\mathrm{e}} \beta_{\mathrm{e}} g_i \beta_{\mathrm{n}} \rho(r_i),$$

where β_{n} is the nuclear magneton, g_{e} is the electronic g-factor, and g_i and $\rho(r_i)$ are the nuclear g-factor and electron spin density at the nucleus, respectively, for nucleus i. Simply put, hfc constants are obtained by multiplying the electronic spin density evaluated exactly at each nucleus i with the appropriate physical constants. As suggested by the form of the Fermi contact term, the connection between spin density and hfcs can also be used in the opposite order, i.e., experimentally determined hfc constants provide a practical means for evaluation of nuclear spin densities.

From the form of the Fermi contact interaction term, it follows that the hfc constants are extremely difficult to calculate theoretically because of their high sensitivity to the quality of the wave function (spin density) at one point in space; the Dirac delta function $\delta(r_i)$ evaluates the wave function only at the nucleus thus making the property very local and unlikely to benefit from error cancellations. Although alternative formulations which use more global operators than the Dirac delta function in calculation of Fermi contact interaction have been introduced [7], none of them have yet found widespread use.

The delta function-based formulation also implies that the Gaussian-type (GTO) basis sets employed in the majority of molecular orbital methods are fundamentally flawed to be used in calculation of Fermi contact interactions [8]. However, it has been shown that, when augmented with tight s-functions, the standard Gaussian-type basis sets can indeed overcome the nuclear cusp problem [9]. An