Thomas-Fermi Theory of the Hyperfine Constants of Endohedral Fullerene Atoms

Joshua Schrier and K. Birgitta Whaley

Department of Chemistry and Pitzer Center for Theoretical Chemistry, University of California, Berkeley, CA 94720

We present a modified Thomas-Fermi theory that describes the increase of the hyperfine coupling constants of endohedrally enclosed atoms. We use the March boundary conditions corresponding to a positively charged spherical shell surrounding the nuclear potential to represent the effect of the fullerene shell. We obtain quantitative agreement with experimental data for N@C_{60} and N@C_{70}, and find that fullerene radius dominates over the fullerene charge in its effect on the hyperfine coupling constants. We also present predictions for the hyperfine coupling constants of the endohedral nitrogen fullerenes between C_{60} and C_{500}, and discuss the implications for proposed quantum computing schemes.

I. INTRODUCTION

The nitrogen endohedral fullerene molecule, N@C_{60}, has received a great deal of experimental\cite{1,2,3,4,5,6,7,8,9} and theoretical\cite{10,11,12} study. Unlike the metallofullerenes, the endohedral nitrogen acts essentially as a “free” atom with a S = 3/2 quartet ground electronic state, although spatially restricted by a harmonic-oscillator-like potential within the fullerene.\cite{1,2,7} Additionally, the fullerene acts as a Faraday cage, shielding the spin of the endohedral nitrogen atom from stray fields\cite{13} and the sharp ESR spectra indicate long spin relaxation times\cite{3} which have inspired its use as a potential spin qubit for quantum computation.\cite{14,15,16,17,18,19,20} Experimental\cite{9} and theoretical\cite{20} studies have indicated that suitable pulse sequences can reduce single qubit errors in these systems to the order of 10^{-6}, which is within the 10^{-4} error threshold of Steane.\cite{21}

An interesting physical phenomenon observed for endohedral atom systems is an increase in the hyperfine coupling constant as compared to its gas phase value, in particular, an increase of 54.1% for N@C_{60} and of 49.1% for N@C_{70}.\cite{22} To better understand the origin of this effect, Kobayashi et al carried out \textit{ab initio} MP2/uc-Hugina+g+(2df) calculations, obtaining enhancements of 77% and 65% for N@C_{60} and N@C_{70}, respectively.\cite{12} In general, quantitative calculation of the hyperfine constant is a difficult problem, even for the free atom.\cite{23} However, a clear qualitative model for the effects of changes in fullerene size and charge that allows prediction of these coupling constants would be helpful, not only for understanding the underlying physics, but also to provide estimates of potential sources of qubit error in applications to quantum information processing. In this paper we introduce a modified Thomas-Fermi
theory for the hyperfine coupling constants in endohedral fullerenes that is capable of quantitatively reproducing the experimental results and provides the desired predictive capabilities. We show that the model is accurate by reproducing the experimentally observed increase in coupling constants for N@C$_{60}$ and N@C$_{70}$. We then analyze the independent roles of fullerene cage size and number of electrons on this enhancement and make predictions for the hyperfine coupling enhancement for nitrogen atoms endohedral to fullerenes between C$_{60}$ and C$_{500}$.

II. THEORY

Following the spherical boundary condition model for highly symmetric molecules developed by March$^{24}$ and later applied to endofullerenes by Clougherty$^{25}$, we treat the fullerene as a sphere of radius $r = R$, contributing $n \pi$-electrons and with a charge of $Ne$, around the nuclear point charge of $Ze$ at the origin. For example, for N@C$_{60}$, $Z = 7$ and $n = 60$. Transforming into the reduced coordinates, $x$, given by $r = bx$ where

$$b = \frac{1}{4} \left( \frac{9\pi^2}{2Z} \right)^{1/3} a_{Bohr}$$

(1)

and $a_{Bohr}$ is the Bohr radius, we transform the cage radius $R \rightarrow X$. We then proceed to solve the usual Thomas-Fermi differential equation$^{26}$

$$\frac{d^2\chi}{dx^2} = \frac{\chi^{3/2}}{x^{1/2}}$$

(2)

with the additional boundary condition$^{24,25}$

$$\chi'(X^-) - \chi'(X^+) = \frac{Z}{nX},$$

(3)

to account for the spherical shell, in addition to a continuity condition, $\chi(X^-) = \chi(X^+)$, and the usual boundary conditions of $\chi(0) = 1$ and $\chi(\infty) = 0$. Clougherty and co-workers$^{25,27}$ have examined the effect of treating the icosahedral (i.e., non-spherical) nature of the fullerene by means of a multipole expansion, but we neglect this effect in the current work.

Next, we use the expression derived by Fermi$^{28,29}$

$$p_l = \frac{4(2l + 1)}{2\pi \hbar} \int_{r_1}^{r_2} 2meV(r) - \left[ \left( l + \frac{1}{2} \right) \hbar r^{-1} \right]^2 dr$$

(4)

which relates the number of electrons, $p_l$, having angular momentum $l$, to the potential, $V(r) = Ze\chi(r)/r$. Other expressions for determining the angular momentum assignments from Thomas-Fermi models have been developed, but give similar results for low $Z$. The limits of integration are chosen so that the integrand (and hence the integral) is
a positive real number. In our case, we take the upper limit of integration to be some tunable cutoff radius, $r_c$, inside the fullerene shell, to count only the endohedral atom electrons and avoid contributions of the fullerene electrons to the integral. We are primarily interested in the number of unpaired $l = 0$ electrons (vide infra). Considering only the “valence” $l = 0$ electrons, there is no ambiguity due to Hund’s rule, as there is for the $l > 0$ electrons, so we may therefore express the number of fractional, i.e., non-integer, number of $l = 0$ electrons as

$$p_{l=0}^{\text{frac}} = \frac{\langle p_{l=0} \rangle}{2}$$

and the number of unpaired $l = 0$ electrons as

$$p_{l=0}^{\text{unpaired}} = \begin{cases} p_{l=0}^{\text{frac}}, & \text{if } p_{l=0}^{\text{frac}} \leq \frac{1}{2} \\ 1 - p_{l=0}^{\text{frac}}, & \text{if } p_{l=0}^{\text{frac}} > \frac{1}{2} \end{cases} \quad (6)$$

The contact-term of the isotropic hyperfine coupling constant,\textsuperscript{32,33}

$$a = \frac{4\pi}{3} g_e g_N \mu_B \mu_N \hbar \langle S_z \rangle^{-1} \langle \Psi | \rho(0) | \Psi \rangle, \quad (7)$$

is proportional to the electron spin-density (difference between spin up and spin down densities) at the nucleus, $\rho(0)$ ($\langle S_z \rangle^{-1}$). However it is well known that the Thomas-Fermi method gives an infinite density at the nucleus, and qualitatively poor results near the nucleus (precluding extrapolation), so a direct evaluation of $\rho(0)$ will fail.\textsuperscript{26} A similar problem occurs in the treatment of the hyperfine coupling constants by semiempirical quantum chemistry methods, in which the 2s and 3s Slater orbital basis functions erroneously have zero density at the nucleus.\textsuperscript{33}

To avoid this problem, we present a heuristic argument in the language of atomic orbital theory. The atom-centered basis functions on a free atom may each be decomposed into a radial function multiplied by a spherical harmonic angular function. For orbitals with $l > 0$, a node occurs at the nucleus, resulting from the properties of the spherical harmonics, so the electrons in these orbitals have no density at the nucleus. This is unchanged when the atom is placed in a spherically symmetric potential, allowing us restrict our attention to the $l = 0$ electrons only. The magnitude of the spin density at the origin, $\rho(0)$, is the product of the probability density of finding an $l = 0$ electron at the origin, times the number of unpaired $l = 0$ electrons, $p_{l=0}^{\text{unpaired}}$, given by Eq.(6). Following the argument made by Pople et al.,\textsuperscript{33} we can consider the basis, and hence the $l = 0$ probability density term, to be unchanged by the chemical surroundings of the atom, and consider the changes to occur only in the basis orbital populations. Similar arguments have been made in the calculation of host medium effects (including endohedral fullerene inclusion) on the $L/K$ electron-capture $\beta$-decay ratio of $^7\text{Be}$.\textsuperscript{34,35} This allows evaluation of the ratio of $\rho(0)$ for the free and endohedral atom cases, as in Eq.(8), below, in which the unknown probability density term now cancels, leaving the ratio in terms of $p_{l=0}^{\text{unpaired}}$, which we can calculate from Eq.(6).
Strictly, the fullerene carbon-atom basis functions may have a small non-zero value at the nitrogen atom nucleus. However, if we make a zero-differential overlap (ZDO) approximation, which is well justified by the lack of a chemical bond between the carbon and nitrogen atoms, this contribution is zero. In our calculation we neglect the contributions from fullerene electrons by considering large fullerenes, and by choosing the cut-off radius $r_c$ used to determine the integral in Eq.(4), to be sufficiently smaller than the cage radius, $R$, but sufficiently large to enclose the region one would chemically attribute to the endohedral atom. We discuss the choice of $r_c$, with particular attention to the difference in applicability for N@C$_{60}$ and P@C$_{60}$ in the next section.

Following the above discussion, the hyperfine compression ratio of Buchachenko$^{22}$ originally given in terms of the endohedral and free atom hyperfine coupling constants $a$ and $a_0$, respectively, may then be expressed as

$$
\phi = \frac{a - a_0}{a_0} = \frac{p_{l=0}^{unpaired}(endohedral) - p_{l=0}^{unpaired}(free)}{p_{l=0}^{unpaired}(free)}
$$

in which a consistent value of $r_c$ is used for the evaluation of both the endohedral and free atom terms, in order to make the probability density for the $l = 0$ electron at the nucleus transferable between the two cases, as discussed above.

### III. RESULTS

To determine the appropriate value of the cut-off radius, $r_c$, we plot calculated values of $\phi$ versus $r_c$ for N@C$_{60}$ and N@C$_{70}$ in Figure II obtained using the experimental fullerene dimensions given by Buchachenko$^{22}$ To match the experimental measurement for N@C$_{60}$ of $\phi = 0.541$, we take $r_c = 3.01$ bohr. This yields values of $\phi = 0.541, 0.562$ and 0.345 for C$_{60}$, for 6.607 bohr radius (short axis) C$_{70}$, and for 7.38 bohr radius (long axis) C$_{70}$, respectively. Since the C$_{70}$ molecule is prolate, the average value of $\phi$ computed by weighting the short axis value twice is 0.490, in excellent agreement with the experimentally measured value of $\phi = 0.491^{22}$. For comparison, we note that the values of $\phi$ evaluated with $r_c = 3.00$ bohr are 0.531 and 0.486 for C$_{60}$ and C$_{70}$ (average value), and also in reasonable agreement with experiment. Our value of $r_c \approx 3$ bohr is consistent with the spatial extent of the spin density distribution determined in the ab initio calculations of Kobayashi et al$^{12}$. However, our attempt to perform a similar calculation for P@C$_{60}$ was unsuccessful, due to the larger size of the P atom. This requires a larger $r_c$ and thus unavoidably introduces possible contributions from fullerene electrons. Thus we restrict the analysis below to nitrogen endohedral fullerenes.
We have examined the relative roles of the number of cage π-electrons, \( n \), and radius, \( R \), on \( \phi \), shown in Figure 2. Intuitively, one expects \( \phi \) to be inversely proportional to fullerene radius \( R \) (at constant number of cage electrons \( n \)), and to be directly proportional to \( n \) (at constant \( R \)). Variations in \( n \) and \( R \) may arise experimentally by endohedral inclusion into defect fullerenes\(^{26,28}\) by use of boron or nitrogen substitutions in place of carbon atoms in the fullerene\(^{26,28}\)
or as the result of interactions with surfaces\(^{39,40}\). In practice, simultaneous variations of \( n \) and \( R \) are unavoidable. Nevertheless, we will analyze ideal independent variations of these two parameters in order to establish their relative importance. The papers by Buchachenko\(^{22}\) and by Kobayashi et al.\(^{12}\) both make the qualitative statement that cage radius (\( R \)) is more important than the cage electrons (\( n \)) in enhancing the hyperfine coupling of the endohedral nitrogen atom. The simplicity of the present model allows us to separate and directly test these two contributions. Figure 2 confirms these statements, as is visible from the much steeper slope of the constant-\( n \) curves (i.e., varying \( R \)), as compared to the constant-\( R \) (i.e., varying \( n \)) curves. For \( \text{N@C}_{60} \), at \( \Delta n = 0 \) and \( \Delta R = 0 \), the slopes are \( d\phi/dR = -0.35 \text{ bohr}^{-1} \) and \( d\phi/dn = 0.0031 \). We discuss the implications of the magnitude of these dependencies for quantum computation in the next section.

To examine the hypothetical endohedral fullerenes \( \text{N@C}_n \) with \( 60 < n < 500 \), most of which have not yet been systematically studied, we have assumed that the ratio of \( n/S \) is constant, where \( S = 4\pi R^2 \) is the surface area of a spherical fullerene. Thus for \( \text{C}_{60} \), \( S = 543 \text{ bohr}^2 \) and \( n/S = 0.11 \); for \( \text{C}_{70} \), \( S = 592 \text{ bohr}^2 \) and \( n/S = 0.12 \). Figure 3 shows the behavior of the hyperfine compression ratio, \( \phi \), for \( \text{N@C}_n \) with \( 60 < n < 500 \), for \( n/S = 0.10, 0.11, \) and \( 0.12 \). As expected, \( \phi \) is seen to be a monotonically decreasing function of \( n \), regardless of the choice of \( S/n \), and asymptotically approaches zero (i.e., the free-atom limit of no enhancement of the hyperfine coupling constant) as the fullerene becomes larger. Depending on the exact value of \( S/n \), we find \( \phi < 0.1 \) for \( 130 \leq n \leq 160 \) and \( \phi < 0.01 \) for \( 350 \leq n \leq 380 \). Even for the hypothetical \( \text{C}_{500} \) fullerene, with a radius of \( \sim 40 \) bohr, we find a finite enhancement of \( 0.002 \leq \phi \leq 0.004 \), which could be detectable experimentally\(^{22}\).

**IV. SUMMARY AND DISCUSSION**

Using a modified Thomas-Fermi theory, we have developed a simple physical model for the effect of endohedral inclusion on the hyperfine coupling constant of nitrogen. The only free parameter in our model is the cutoff radius, \( r_c \), used to partition the atom from the fullerene. A single choice of \( r_c \approx 3.0 \) bohr is found to give quantitative agreement with recent experimental results for both \( \text{N@C}_{60} \) and \( \text{N@C}_{70} \). Moreover, the simplicity of our model allows us to separate the relative contributions of cage potential and size on the hyperfine coupling constants, and to thereby
identify the fullerene radius as the dominating factor in the scaling of the hyperfine compression ratio $\phi$. We have also predicted the hyperfine coupling constants for nitrogen endohedral to hypothetical fullerenes as large as C$_{500}$ and find that a finite enhancement should exist up to this size.

Spin exchange between the electron and nuclear degrees of freedom mediated by the hyperfine interaction is necessary to implement the quantum cellular automata scheme of Twamley.$^{15,16}$ Since global operations on all the qubits are used to evolve the computational unitary in this scheme, deviations in the hyperfine coupling constants of the individual sites, e.g. due to deformations resulting from fullerene interaction with the substrate surface, would require additional complication in the nuclear-electronic CNOT and swap operations in order to be robust against these variations. Our results in Section III indicate that the hyperfine coupling is quite sensitive to these deformations, and that even a 1% (0.07 Å) change in the N@C$_{60}$ radius would result in a $\sim 5\%$ change in the compression ratio $\phi$, corresponding to an approximately 0.5 MHz shift in the hyperfine constant. Using the fidelity measure $F = |\text{Tr}(VU^\dagger)|/\text{Tr}(UU^\dagger)$, where $U$ is the desired unitary and $V$ is the actual (erroneous) unitary$^{20}$ a 0.5 MHz shift away from the nominal hyperfine interaction gives $1 - F = 2 \times 10^{-4}$ for the electron-nuclear CNOT operation. Atomistic calculations treating the fullerene-surface interactions in more detail, may provide useful estimates for the extent of this deformation on experimentally relevant surfaces.

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FIG. 1: Hyperfine compression ratio, $\phi$, as a function of cutoff radius, $r_c$. For $r_c = 3.01$ bohr, the compression ratios calculated for N@C$_{60}$ and the appropriate weighted average for N@C$_{70}$ are 0.541 and 0.490, respectively, in excellent agreement with the experimental values 0.541 for N@C$_{60}$ and 0.491 for N@C$_{70}$.

FIG. 2: Effects of changing $n$ (positive slope curves) and $R$ (negative slope curves) for C$_{60}$ ($n_0 = 60, R_0 = 6.578$ bohr) and a spherical model C$_{70}$ ($n_0 = 70, R_0 = 6.8647$ bohr) on the hyperfine compression ratio $\phi$. Here $n = n_0 + \Delta n$ and $R = R_0 + \Delta R$, where $n_0$, $R_0$ are the equilibrium values of $n$ and $R$, respectively. For C$_{60}$ at $\Delta n = 0$ and $\Delta R = 0$, $d\phi/dn = 0.0031$ and $d\phi/dR = -0.35$ bohr$^{-1}$. 
FIG. 3: Values of the hyperfine compression ratio, $\phi$, for the N@C$_n$ with $60 < n < 500$, assuming surface charge/area ratios, $n/S$, of 0.10, 0.11, and 0.12.