

Computations of Small Physical Effects in Nuclear Magnetic Resonance

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Despite that NMR computations have become routine in much of modern spectroscopy, interesting physical NMR phenomena remain. I introduce four distinct topics.

1. J -couplings over van der Waals (vdW) bonds have been computed [1]. There has only been one direct and one indirect observation, for $J(^{129}\text{Xe}-^1\text{H})$ in pentane(*l*) [2] and $\Delta J(\text{Xe}-\text{Xe})$ in a zeolite [3], respectively. $J(^{129}\text{Xe}-^3\text{He})$ measured in a gas-phase co-magnetometer [4] can now be quantitatively calculated [5] involving the virial coefficient of relativistic J -coupling. $J(^{129}\text{Xe}-^3\text{He})$ is vast compared to the sub-nHz physics sought with co-magnetometers.
2. Increasing B_0 -field strengths in modern NMR render its parameters [6] field dependent. Only for ^{131}Xe quadrupole coupling [7,8] has this been verified [8,9]. ^{59}Co shift in $\text{Co}(\text{acac})_3$ is rendered B_0 -dependent by low-lying d-d excitations [10]. The leading $O(B_0^2)$ non-linear response terms [11] are evaluated presently.
3. Nuclear magneto-optics (NMO) prospect sensitive optical detection of nucleus-specific data. Therein, light polarisation is altered by molecular electrons interacting with nuclear spins. The phenomena include nuclear spin optical rotation (expt. [12], theory [13]), its dichroism, spin- and quadrupole-induced Cotton-Mouton (CM) effects, as well as spin-CM in the presence of B_0 [14]. We predict nuclear spin-induced magnetochiral birefringence and dichroism, possible reporters of chirality via the difference of the refractive index for light propagating parallel and antiparallel to nuclear spin magnetisation [15].
4. In spin-exchange optical pumping, polarisation is transferred from optically polarised Rb to noble gas nuclei in gas [16]. We extract from molecular dynamics a large number of Rb-Xe interaction events, and analyse them using spin dynamics driven by quantum-chemical spin Hamiltonian [17]. We reproduce the roles of binary collisions and long-lived vdW complexes in the transfer and witness a step-wise build-up of ^{129}Xe polarisation upon vdW oscillations.

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