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Theoretical and Physical Aspects of Nuclear Shielding

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A. General Theory — The general concept of nuclear shielding in the presence of electromagnetic radiation is introduced by defining dynamic electromagnetic shielding tensors which describe the linear response in an external spatially uniform periodic electromagnetic field.[1] The diamagnetic terms do not depend on the angular frequency, ω, of the electromagnetic radiation. The dynamic paramagnetic shielding tensor is a generalization of Ramsey's definition for the static property.

The magnetic field induced by the electrons at nucleus I is expressed by Lazzeretti and Zanasi as follows[1]:

$$\mathbf{B}_{\text{induced}} = -\left(\sigma^p + \sigma^d\right)\cdot\mathbf{B} - \hat{\sigma}^p\cdot\dot{\mathbf{B}} + \lambda^I\cdot\mathbf{E} + \hat{\lambda}^I\cdot\dot{\mathbf{E}} \qquad (1)$$

The external magnetic field $\mathbf{B}$ is the real part of $\mathbf{B}_0\ \exp(i\omega t)$. $\dot{\mathbf{B}}$ is the partial derivative with respect to time. In the first term, σ^p is the dynamic paramagnetic shielding tensor,

$$\sigma^p(\omega) = \left(\frac{\mu_0}{4\pi}\right)\cdot\frac{-e^2}{2m^2\hbar}\sum_{j\neq a}\frac{2\omega_{ja}}{\omega_{ja}^2-\omega^2}\times \mathrm{Re}\left(\langle a|\mathbf{M}_I|j\rangle\langle j|\mathbf{L}|a\rangle\right) \qquad (2)$$

in which $\mathbf{L}$ and $\mathbf{M}_I$ involve the usual angular momentum operators $\ell_i(\mathbf{R}_I)$ centered on I and ℓ_i at the gauge origin.

$$\mathbf{M}_I = \sum_i\frac{\ell_i(\mathbf{R}_i)}{|\mathbf{r}_i-\mathbf{R}_I|^3} \qquad \mathbf{L} = \sum_i \ell_i \qquad (3)$$

and $|a\rangle$ and $|j\rangle$ are the time-independent perturbed states which are functions of $\mathbf{B}_0$. σ^d is the same as Ramsey's, and the $\hat{\lambda}^I(\omega)$ term is called magnetoelectric shielding. Its physical meaning is shown in the equation; by taking the scalar diadic product with the time derivative of external electric field, one obtains the magnetic field induced at the nucleus. The terms in $\hat{\sigma}^p$ and λ^I give the magnetic fields induced at the nucleus by a time-dependent magnetic field and an external electric field, respectively. $\lambda^I(\omega)$ is the analogous definition to $\sigma^p(\omega)$, except that $\mathbf{L}$ is replaced by $-2mc\mathbf{R}$, $\mathbf{R}$ being $\sum_i r_i$. $\hat{\sigma}^p(\omega)$ takes the imaginary part, whereas σ^p has the real part of the complex integrals $\langle a|\mathbf{M}_I|j\rangle\langle j|\mathbf{L}|a\rangle$ and $\hat{\lambda}^I$ takes the imaginary part, while λ^I has the real part of the complex integrals $\langle a|\mathbf{M}_I|j\rangle\langle j|\mathbf{R}|a\rangle$. The generalized