

395 (1): Effect of the Vacuum on the Permittivity Shift  
 Consider the nuclear vector potential of a nucleus in a molecule:

$$\underline{A}_N = \frac{\mu_0}{4\pi r^3} \underline{m}_N \times \underline{r} \quad - (1)$$

where  $\underline{m}_N$  is the nuclear magnetic dipole moment. The interaction Hamiltonian is:

$$H = \frac{1}{2m} (\underline{p} + e\underline{A}_N) \cdot (\underline{p} + e\underline{A}_N) + U. \quad - (2)$$

The first order interaction Hamiltonian is:

$$H^{(1)} = \frac{e}{2m} (\underline{p} \cdot \underline{A}_N + \underline{A}_N \cdot \underline{p}) \quad - (3)$$

and the second order interaction Hamiltonian is:

$$H^{(2)} = \frac{e^2}{2m} \underline{A}_N^2 \quad - (4)$$

From eq. (1):  $\underline{\nabla} \cdot \underline{A}_N = 0 \quad - (5)$

So:

$$\begin{aligned} H^{(1)}\psi &= -\frac{ie\hbar}{2m} (\underline{\nabla} \cdot \underline{A}_N + \underline{A}_N \cdot \underline{\nabla})\psi \\ &= -\frac{ie\hbar}{2m} (\underline{\nabla} \cdot (\underline{A}_N\psi) + \underline{A}_N \cdot \underline{\nabla}\psi) \\ &= -\frac{ie\hbar}{2m} ((\underline{\nabla} \cdot \underline{A}_N)\psi + \underline{A}_N \cdot \underline{\nabla}\psi + \underline{A}_N \cdot \underline{\nabla}\psi) \\ &= -\frac{ie\hbar}{m} \underline{A}_N \cdot \underline{\nabla}\psi \quad - (6) \end{aligned}$$

On the classical level:

$$H^{(1)} = \frac{e}{m} \underline{A}_N \cdot \underline{p} \quad - (7)$$

This can be expressed as:

$$H^{(1)} = - \int \underline{A}_N \cdot \underline{j}_{\text{ext}} d\tau \quad - (8)$$

where

$$\underline{j}_{\text{ext}} = - \frac{e}{2m_e} \left( \phi^* \underline{p} \phi + \phi \underline{p}^* \phi^* \right) \quad - (9)$$

is the current density operator describing the current induced by the applied magnetic field. The interaction between this current and the nuclear magnetic dipole moment produces the chemical shift. This is the most important feature of NMR and also ESR.

From eqs. (1) and (9):

$$H^{(1)} = - \frac{\mu_0}{4\pi} \int \frac{\underline{m}_N \times \underline{r}}{r^3} \cdot \underline{j}_{\text{ext}} d\tau \quad - (10)$$

$$= - \frac{\mu_0}{4\pi} \underline{m}_N \times \int \frac{1}{r^3} \underline{r} \cdot \underline{j}_{\text{ext}} d\tau$$

$$= - \frac{\mu_0}{4\pi} \underline{m}_N \cdot \int \left( \frac{\underline{r} \times \underline{j}_{\text{ext}}}{r^3} \right) d\tau$$

$$= - \underline{m}_N \cdot \underline{B}'$$

where  $\underline{B}'$  is the magnetic flux density of the chemical shift:

$$\underline{B}' = \frac{\mu_0}{4\pi} \int \frac{\underline{r} \times \underline{j}_{\text{ext}}}{r^3} d\tau \quad - (11)$$

In chemical shift theory this is defined in terms of the shielding constant  $\sigma$ :

$$3) \quad \sigma \underline{B} = -\frac{\mu_0}{4\pi} \int \frac{\underline{r} \times \underline{j}_{\text{ext}}}{r^3} d\tau \quad - (12)$$

So the local magnetic flux density is:

$$\underline{B}_{\text{local}} = \underline{B}(1-\sigma) \quad - (13)$$

where  $\underline{B}$  is the externally applied magnetic flux density of the nuclear magnetic resonance spectrometer.

Therefore:

$$\begin{aligned} E^{(1)} &= -i e \hbar \int \psi^* \underline{A}_N \cdot \underline{\nabla} \psi d\tau \\ &= -\frac{m}{m} \cdot \frac{\mu_0}{4\pi} \int \frac{\underline{r} \times \underline{j}_{\text{ext}}}{r^3} d\tau \end{aligned} \quad - (14)$$

The effect of the vacuum on eq. (1) is to change it to:

$$\begin{aligned} \underline{A}_N(\underline{r} + \delta \underline{r}) &= \frac{\mu_0}{4\pi |\underline{r} + \delta \underline{r}|^3} \underline{m}_N \times (\underline{r} + \delta \underline{r}) \\ &= \frac{\mu_0}{4\pi r^3} \underline{m}_N \times (\underline{r} + \delta \underline{r}) \left( 1 - \frac{3x}{2} + \frac{15}{8} x^2 + \dots \right) \quad - (15) \end{aligned}$$

The magnetic field of the chemical shift is changed to:

$$\underline{B}'(\underline{r} + \delta \underline{r}) = \frac{\mu_0}{4\pi} \int \frac{(\underline{r} + \delta \underline{r}) \times \underline{j}_{\text{ext}}}{|\underline{r} + \delta \underline{r}|^3} d\tau \quad - (16)$$

$$= \frac{\mu_0}{4\pi} \int \left( \frac{\underline{r} \times \underline{j}_{\text{ext}}}{r^3} \right) \left( 1 - \frac{3x}{2} + \frac{15}{8} x^2 + \dots \right) d\tau$$

$$4) + \int \left( \frac{\underline{\delta r} \times \underline{j}_{\text{rot}}}{r^3} \right) \left( 1 - \frac{3x}{2} + \frac{15}{8}x^2 + \dots \right) d\tau$$

Comparing eqs (11) and (16) it becomes clear that vacuum fluctuations affect the chemical shift, and are observable in NMR.

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