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Nuclear spin–rotation interaction and non-Abelian gauge potential

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It is shown that nuclear spin–rotation interaction in diamagnetic systems with $I = \frac{1}{2}$ appears as a manifestation of a $U(2)$ non-Abelian gauge potential and can be represented in purely geometric terms as a consequence of the corresponding non-Abelian connection.

It has been shown that molecular rotation representing an adiabatic perturbation to the electronic Hamiltonian generates a non-trivial gauge potential which leads to a geometric phase of a state vector [1]. The appearance of such a gauge potential in diatomics, first demonstrated by Moody *et al.* [2], has been considered by Zygelman [3] and in greater detail by Bohm *et al.* [4]. Very recently, it has been shown [5] that electron spin–rotation (SR) interaction in *paramagnetic* molecular systems with an effective spin $S_{\text{eff}} = \frac{1}{2}$ can be represented in terms of a $U(2)$ non-Abelian gauge potential. It is the purpose of this article to elucidate the non-Abelian gauge structure of *nuclear* SR interaction in rotating *diamagnetic* molecules, which have neither resultant electronic spin S nor electronic orbital momentum L.

We begin by consideration of the response of a quantum system with a Kramers doublet ground state to an adiabatic variation of the Hamiltonian $H[\Omega(t)]$ along the closed path $\Omega(t)$ in the angular space. In this case the evolution of the system can be described in terms of the effective Hamiltonian H_{eff} (in general a 2×2 matrix). Following Wilczek and Zee [6], we can represent H_{eff} in the moving (M) frame of reference attached to the rotating internal framework in the following form:

$$[H^{(\text{M})}_{\text{eff}}]_{mm'} = -i\langle\tilde{\chi}^{(\text{M})}_{1/2,m}[\Omega(t)]|\left(\frac{\text{d}}{\text{d}t}|\tilde{\chi}^{(\text{M})}_{1/2,m'}[\Omega(t)]\rangle\right) \quad (m, m' = \pm\tfrac{1}{2}), \tag{1}$$

where $|\tilde{\chi}^{(\text{M})}_{1/2,m}[\Omega(t)]\rangle$ represents one of the two degenerate eigenvectors belonging to the lowest eigenvalue of the instantaneous Hamiltonian $H^{(\text{M})}[\Omega(t)]$. Since a two-dimensional quantum space is dealt with by the formalism of effective spin $S_{\text{eff}} = \frac{1}{2}$, we will use the set of quantum numbers $\frac{1}{2}$, $\pm\frac{1}{2}$ (S_{eff}, $S_{z,\text{eff}}$ whereby the quantization axis z refers to the M frame, cf. [5]). Furthermore, here and in the following the convention $\hbar = 1$ will be used.

Starting with $|\tilde{\chi}^{(\text{L})}_{1/2,m}[\Omega(0)]\rangle$ ($\Omega(0) = 0$) which is an eigenvector of the lowest eigenstate of the true Hamiltonian at $t = 0$, we may define a family of instantaneous eigenfunctions of $H^{(\text{M})}[\Omega(t)] = R[\Omega(t)]H^{(\text{L})}(0)R^{-1}[\Omega(t)]$ at the moment t by a rotation operator $R[\Omega(t)]$:

$$|\tilde{\chi}^{(\text{M})}_{1/2,m}[\Omega(t)]\rangle = R[\Omega(t)]|\tilde{\chi}^{(\text{L})}_{1/2,m}[\Omega(0)]\rangle. \tag{2}$$

Here (L) denotes the initial molecular frame.

To proceed further, we first specify the differential action of $H_{\mathrm{eff}}^{(\mathrm{M})}$:

$$H_{\mathrm{eff}}^{(\mathrm{M})}\,\mathrm{d}t \equiv -\boldsymbol{A}^{(\mathrm{M})}\cdot \mathrm{d}\boldsymbol{\Omega}, \tag{3}$$

where

$$A_{mm'}^{(\mathrm{M})} = i\langle \tilde{\chi}_{1/2,m}^{(\mathrm{M})}[\Omega(t)]|\nabla_{\Omega}|\tilde{\chi}_{1/2,m'}^{(\mathrm{M})}[\Omega(t)]\rangle \tag{4}$$

is the corresponding $U(2)$ non-Abelian gauge potential [1].

At this stage it is necessary to specify the set of parameters necessary to define the actual position of the system in the angular space at time t and the differential change of the orientation of the M frame which occurs at this moment. To define the position, the Eulerian angles are most appropriate. For the differential change, however, it is more convenient to define $\mathrm{d}\Omega = \{\delta\phi_{\boldsymbol{n}}, \boldsymbol{n}\}$, where $\boldsymbol{n}$ denotes the unit vector along the instantaneous axis of rotation in the molecular frame at time t, and $\delta\phi_{\boldsymbol{n}}$ is the angle of infinitesimal rotation around it. That allows us to represent the scalar product in equation (3) in the following form

$$A^{(\mathrm{M})}\,\mathrm{d}\Omega = -A_{\boldsymbol{n}}^{(\mathrm{M})}\delta\phi_{\boldsymbol{n}}, \tag{5}$$

where

$$(A_{\boldsymbol{n}}^{(\mathrm{M})})_{mm'}\delta\phi_{\boldsymbol{n}} = i\langle \tilde{\chi}_{1/2,m}^{(\mathrm{M})}[\Omega(t)]|\left(\frac{\partial}{\partial\phi}\right)_{\boldsymbol{n}}|\tilde{\chi}_{1/2,m'}^{(\mathrm{M})}[\Omega(t)]\rangle\delta\phi_{\boldsymbol{n}}. \tag{6}$$

Note that, while a sequence of $\{\delta\phi_{\boldsymbol{n}}, \boldsymbol{n}\}$ values uniquely defines the path of the molecule in the orientational space, $\delta\phi_{\boldsymbol{n}}$ is not an exact differential, i.e. $\phi_{\boldsymbol{n}}$ is not a genuine coordinate uniquely related to the path in the angular space.

The effect of $(\partial/\partial\phi)_{\boldsymbol{n}}\delta\phi_{\boldsymbol{n}}$ is to rotate the molecular axes from Ω to $(\Omega + \mathrm{d}\Omega)$, whereby the eigenfunction $|\tilde{\chi}_{1/2,m}^{(\mathrm{M})}[\Omega(t)]\rangle$ is changed to

$$|\tilde{\chi}_{1/2,m}^{(\mathrm{M})}[\Omega(t) + \mathrm{d}\Omega]\rangle = [1 - i\delta\phi_{\boldsymbol{n}}\boldsymbol{n}(\theta, \varphi)\boldsymbol{J}]|\tilde{\chi}_{1/2,m}^{(\mathrm{M})}[\Omega(t)]\rangle. \tag{7}$$

Here $\boldsymbol{J}$ is the total angular momentum operator of the system defined with respect to the axes of the M frame at time t. Thus, equation (6) can be expressed as

$$\begin{aligned}(A_{\boldsymbol{n}}^{(\mathrm{M})})_{mm'}\delta\phi_{\boldsymbol{n}} &= i\langle \tilde{\chi}_{1/2,m}^{(\mathrm{M})}[\Omega(t)]|\tilde{\chi}_{1/2,m'}^{(\mathrm{M})}[\Omega(t) + \mathrm{d}\Omega]\rangle - i\langle \tilde{\chi}_{1/2,m}^{(\mathrm{M})}[\Omega(t)]|\tilde{\chi}_{1/2,m'}^{(\mathrm{M})}[\Omega(t)]\rangle \\ &= \delta\phi_{\boldsymbol{n}}\boldsymbol{n}\langle \tilde{\chi}_{1/2,m}^{(\mathrm{M})}[\Omega(t)]|\boldsymbol{J}|\tilde{\chi}_{1/2,m'}^{(\mathrm{M})}[\Omega(t)]\rangle.\end{aligned} \tag{8}$$

Using the set of Pauli matrices $\boldsymbol{\sigma}$ we may express the 2×2 matrix of $\boldsymbol{J}$ (equation (8)) in the following general form (see also [5])

$$\langle \tilde{\chi}_{1/2,m}^{(\mathrm{M})}[\Omega(t)]|\boldsymbol{J}|\tilde{\chi}_{1/2,m'}^{(\mathrm{M})}[\Omega(t)]\rangle \equiv \tfrac{1}{2}\hat{\gamma}[\Omega(t)]\boldsymbol{\sigma}_{mm'}, \tag{9}$$

whereby, a tensor $\hat{\gamma}[\Omega]$ is defined. Note that all the relevant information about the original 'unrotated' Hamiltonian $H^{(\mathrm{M})}(0) = H^{(\mathrm{L})}(0)$ which comprises the actual physical problem is now represented by the $\hat{\gamma}$ tensor. The original Hamiltonian serves only to determine the gauge group and the principal values of $\hat{\gamma}$. At the moment $t = 0$ the basis functions $|\tilde{\chi}_{1/2,m}^{(\mathrm{M})}[\Omega(0)]\rangle = |\tilde{\chi}_{1/2,m}^{(\mathrm{L})}[\Omega(0)]\rangle$ may always be chosen such that $\hat{\gamma}$ is diagonal and that the main axis z of this 'tensor' represents the quantization axis of the effective spin operator $\boldsymbol{\sigma}/2$. If $|\tilde{\chi}_{1/2,m}\rangle$ were a pure spin doublet $|\chi_{1/2,m}\rangle$, then these functions would span a complete representation of the spinor group $SU(2)$ $(J = S)$ and $\hat{\gamma}$ would become the unit matrix. Any coupling of the spin to other degrees of freedom associated with orbital angular momentum will be reflected in a non-unit γ tensor.

Substituting equation (9) into (8) we arrive at

$$H^{(\mathrm{M})}_{\mathrm{eff}}\,\mathrm{d}t = -A^{(\mathrm{M})}_{\boldsymbol{n}}\delta\phi_{\boldsymbol{n}} = -\delta\phi_{\boldsymbol{n}}\boldsymbol{n}\hat{\gamma}[\Omega(t)]\boldsymbol{\sigma}/2. \tag{10}$$

According to this result it is clear that the differential action of $H^{(\mathrm{M})}_{\mathrm{eff}}$ is proportional to $\delta\phi_{\boldsymbol{n}}$, i.e. to the distance in the angular space, independent of the time it takes to perform this rotation. Such behaviour is necessarily expected if the time variation of the true Hamiltonian $H[\Omega(t)]$ is in the adiabatic limit. Using the definition of angular velocity $\boldsymbol{\omega} = \dot{\phi}_{\boldsymbol{n}}\boldsymbol{n}$ we may now represent equation (1) in the following form

$$H^{(\mathrm{M})}_{\mathrm{eff}} = -\boldsymbol{\omega}\hat{\gamma}[\Omega(t)]\boldsymbol{\sigma}/2. \tag{11}$$

For axially symmetric systems J_z commutes with $H^{(\mathrm{L})}(0)$. As a result, in this particular case $\hat{\gamma}_{zz} \equiv \gamma_{\parallel} = 1$, $\hat{\gamma}_{xx} = \hat{\gamma}_{yy} \equiv \gamma_{\perp}$ and equation (11) can be represented in the Wilczek–Zee form [2, 5, 6, 8]:

$$\begin{aligned} H^{(\mathrm{M})}_{\mathrm{eff}} &= -[\omega_z\sigma_z + \gamma_{\perp}(\omega_x\sigma_x + \omega_y\sigma_y)]/2 \\ &= -[\dot{\beta}\gamma_{\perp}\sigma_y + \dot{\alpha}(-\gamma_{\perp}\sigma_x \sin\beta + \sigma_z\cos\beta)]/2, \end{aligned} \tag{12}$$

where $\{\alpha, \beta\}$ is a set of spherical angles defining the orientation of the C_∞ axis of symmetry.

It is easy to represent H_{eff} in the L frame [5]:

$$H^{(\mathrm{L})}_{\mathrm{eff}} = -\boldsymbol{\omega}\delta\hat{\gamma}[\Omega(t)]\boldsymbol{\sigma}/2, \tag{13}$$

where $\delta\hat{\gamma} \equiv \hat{\gamma} - \hat{1}$. This equation shows that in the L frame a response of a Kramers doublet to an adiabatic rotation of the molecular framework can be described as the interaction of an effective spin $\boldsymbol{\sigma}/2$ with a 'fictitious' magnetic field $\boldsymbol{f} = -\boldsymbol{\omega}\delta\hat{\gamma}$. From the definition of $\hat{\gamma}$ given by equation (9), one may conclude that unless the Kramers doublet spans a complete representation of the $SU(2)$ group, which is generally not the case, the field $\boldsymbol{f}$ is not zero. This field appears as a manifestation of the $U(2)$ non-Abelian gauge potential, equation (4).

Equation (13) can be applied to any case of an adiabatically rotated Kramers doublet. Formally, it has the same structure as the spin Hamiltonian H_{sr} of SR interaction for systems with an effective spin $\frac{1}{2}$. It has been shown in [5] that, e.g. for linear radicals, the electron (E) SR tensor can be represented in the following form

$$\hat{C}_{\mathrm{sr,E}} = -2B\delta\hat{\gamma}_{\mathrm{E}}, \tag{14}$$

where B is the rotational constant of a linear rotator. It was also shown [5] that to first order in electron spin–orbit coupling

$$\delta\hat{\gamma}_{\mathrm{E}} = \delta\hat{g} \tag{15}$$

where $\delta\hat{g} = \hat{g} - g_e\hat{1}$ corresponds to the deviation of the components of the g tensor from the value of the free electron.

With the general effective Hamiltonian equation (13) determined, we can now consider quite a different physical system, namely a diamagnetic molecule with one magnetic nucleus with spin $I = \frac{1}{2}$. In this case the full 'unrotated' electronic Hamiltonian (including nuclear spin) can be written as

$$H = T + V + H(L, S) + H(L, I) + H(S, I). \tag{16}$$

Here, T and V represent the kinetic and electrostatic potential energy of the electrons, respectively. The electron spin–orbit coupling $H(L, S)$ and hyperfine coupling $H(S, I)$ can be omitted in the subsequent consideration since the effects of electronic spin in diamagnetic substances are usually orders of magnitude smaller than the contribution of the direct magnetic interaction between the electronic orbital momentum and the nuclear spin $H(L, I)$ (see, e.g. [9] and [10]). Due to this term the ground state vector of H (equation (16)) cannot be represented as a direct product of an electronic space part with a nuclear spin part. Taking into account the interaction $H(L, I)$, the modified eigenfunctions can be represented in the following form:

$$|\tilde{\chi}^{(\mathrm{M})}_{1/2,m}(0)\rangle = |\chi^{(\mathrm{M})}_{1/2,m}(0)\rangle|0\rangle + |\chi^{(\mathrm{M})}_{1/2,m'}(0)\rangle \sum_n{}' a_n|n\rangle, \tag{17}$$

where $|\chi^{(\mathrm{M})}_{1/2,m}(0)\rangle$ is a pure nuclear state, $|0\rangle$ is the orbital wavefunction of the electronic ground state and $|n\rangle$ denotes the nth orbital excited electronic state admixed with coefficient a_n. The corresponding equation applies for the Kramers conjugate state $|\tilde{\chi}^{(\mathrm{M})}_{1/2,m'}(0)\rangle$.

In molecules the electrostatic interaction V has symmetry lower than spherical. Therefore, the mixed states $|\tilde{\chi}^{(\mathrm{M})}_{1/2,m}(0)\rangle$ of the corresponding Kramers doublet neither span a complete representation of the spinor group $SU(2)$ nor of the $SU(2) \times SO(3)$ double group.

Due to a largely different order of magnitude $\|T + V\| \gg \|H(L; I)\|$ a simple perturbation treatment is appropriate. In the lowest non-zero order of perturbation theory, equations (9) and (17) give

$$\tfrac{1}{2}\delta\hat{\gamma}_{\mathrm{N}}(0)\boldsymbol{\sigma}_{mm'} = \sum_n{}' \frac{\langle 0|\boldsymbol{L}|n\rangle\langle n, \chi^{(\mathrm{M})}_{1/2,m}(0)|H(L, I)|0, \chi^{(\mathrm{M})}_{1/2,m'}(0)\rangle}{\Delta_{0n}} + c.c. \tag{18}$$

Here $\Delta_{0n} = E_0 - E_n$ is the energy gap between the eigenstates of electronic Hamiltonian $T + V$.

With the result appearing on the RHS of equation (18) we have arrived at the standard expression used in calculation of nuclear (N) SR interaction and magnetic field shielding in diamagnetic molecules [9, 10]. However, the way it has been derived here is new.

In the one-electron approximation

$$H(L, I) = 2\beta\beta_{\mathrm{N}} \sum_{a,i} g_{\mathrm{N},a} r_{a,i}^{-3} \boldsymbol{l}_{a,i} \boldsymbol{I}_a, \tag{19}$$

where one-electron orbital angular momentum operators $\boldsymbol{l}_{a,i}$ have their origin at the center of the ath nucleus, and β, β_{N}, $g_{\mathrm{N},a}$, $r_{a,i}^{-3}$ have their usual meanings [9, 10], we immediately obtain

$$(\delta\hat{\gamma}_{\mathrm{N}})_{q,q'} = \sum_a (\delta\hat{\gamma}^a_{\mathrm{N}})_{q,q'} = 2\beta\beta_{\mathrm{N}} \sum_{a,i,j} g_{\mathrm{N},a} r_{a,i}^{-3} \sum_n{}' \left(\frac{\langle 0|(\boldsymbol{l}_{a,j})_q|n\rangle\langle n|(\boldsymbol{l}_{a,i})_{q'}|0\rangle}{\Delta_{0n}} + c.c \right). \tag{20}$$

Here q and q' denote the components of $\boldsymbol{l}_{a,i}$ along the corresponding Cartesian axes. Substituting this equation into equation (13), where $\boldsymbol{\sigma}/2$ can be treated now as the effective nuclear spin operator, and comparing the result with the expression for the nuclear SR Hamiltonian obtained by Flygare [11]:

$$H_{\mathrm{sr,N}} = (2\hat{B})^{-1}\boldsymbol{\omega} \sum_a \hat{C}^a_{\mathrm{sr,N}} \boldsymbol{I}_a, \tag{21}$$

$$\hat{C}^a_{\mathrm{sr,N}} = \hat{C}^a_{\mathrm{sr,N}}(1) + \hat{C}^a_{\mathrm{sr,N}}(2) \tag{22}$$

yields the following correspondence for symmetric-top molecules

$$\hat{C}^a_{\mathrm{sr,N}}(2) = -2\hat{B}\delta\hat{\gamma}^a_{\mathrm{N}}. \tag{23}$$

Symmetric-top molecules have at least a C_{3v} axis of symmetry [11]. This axis is chosen here to coincide with the z axis of the L frame, which makes the tensors $\hat{C}_{\mathrm{sr,N}}$, $\hat{B}$ and $\delta\hat{\gamma}_{\mathrm{N}}$ simultaneously diagonal. The first term, $\hat{C}^a_{\mathrm{sr,N}}(1)$, is known to be determined completely by the electronic wavefunction of the ground state [11, 12]. It reflects the appearance of a magnetic field in a molecule rotating as a rigid body. The second term, $\hat{C}^a_{\mathrm{sr,N}}(2)$, arises from the lack of spherical symmetry of the electric field potential V, and is due to the admixture of higher states with the coupled electronic-orbital/nuclear-spin wavefunction which has to adjust itself as the molecule rotates [13, 5].

It should be stressed that $\hat{\sigma}^a_{\mathrm{p}}$ the paramagnetic part of the magnetic shielding tensor [9–12] has the same second order dependence as $\delta\hat{\gamma}^a_{\mathrm{N}}$, equation (20). That allows us to write the following expression relating these two quantities:

$$\delta\hat{\gamma}^a_{\mathrm{N}} = \frac{\beta_{\mathrm{N}} g_{\mathrm{N},a}}{\beta}\hat{\sigma}^a_{\mathrm{p}}. \tag{24}$$

The similarity of equations (14) and (23), (15) and (24) is obvious. It is apparent that $\delta\hat{\gamma}^a_{\mathrm{N}}$ can be eliminated from equations (23) and (24). That gives the traditional result (see, e.g. [14])

$$\hat{C}^a_{\mathrm{sr,N}}(2) = -2\hat{B}\frac{\beta_{\mathrm{N}} g_{\mathrm{N},a}}{\beta}\hat{\sigma}^a_{\mathrm{p}}. \tag{25}$$

What is new in the formulation presented here is that the 'paramagnetic' part of nuclear SR interaction ($\propto \hat{C}^a_{\mathrm{sr,N}}(2)$) appears as a manifestation of the $U(2)$ non-Abelian gauge potential. Note that effective Hamiltonians of nuclear and electron SR interaction have the same gauge structure. Therefore, from the geometric point of view, the treatment of electron SR interaction (as well as relaxation, see [15, 16]) in paramagnetic spin $\frac{1}{2}$ systems is equivalent to the description of nuclear SR interaction (relaxation) in diamagnetic molecules with $I = \frac{1}{2}$.

It should be clear from the above that the non-Abelian gauge structure of nuclear spin–rotation interaction is fundamentally connected with the admixture of 'fast' electron orbital degrees of freedom with the nuclear spin wavefunction induced by the interaction between the electron orbital momentum and nuclear spin. The states that are coupled together by $H(L, I)$ to form the lowest effective nuclear spin doublet have energy separations that are typical of electronic excitation and therefore high frequencies will characterize the time dependent response of the system to any motionally induced perturbation (as, e.g. thermal molecular rotation) acting towards a change in the mixing coefficients of the zero order wavefunctions (see also [5, 15, 16]). As a result, the components of the effective nuclear spin doublet are isolated adiabatically from the higher eigenstates of the molecular Hamiltonian, i.e. effective nuclear spin follows the rotation of the molecule adiabatically.

The main physical difference between nuclei with spin $\frac{1}{2}$ and electrons results from the large nuclear mass. Due to this fact the spin–orbit coupling of a nuclear spin with nuclear orbital motion is negligible in comparison with the coupling with the orbital magnetic momentum of an electron $H(L, I)$. In the first non-zero order of perturbation theory, using the one-electron approximation, it is easy to make the following estimation

$$\frac{\hat{C}^{a}_{\mathrm{sr,N}}(2)}{\hat{C}^{a}_{\mathrm{sr,E}}} = \frac{\delta\hat{\gamma}^{a}_{\mathrm{N}}}{\delta\hat{\gamma}^{a}_{\mathrm{E}}} = \frac{\beta_{\mathrm{N}} g_{\mathrm{N},a}}{\beta Z_{a}} \ll 1, \tag{26}$$

where Z_a is the nuclear charge of the ath nucleus. Alternatively, one may conclude that due to the large nuclear mass the gauge field which governs the evolution of the adiabatically rotated Kramers doublet is much smaller for nuclei than for electrons.

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References

[1] Shapere, A., and Wilczek, F., 1989, *Geometric Phase in Physics* (Singapore: World Scientific); Zwanziger, J. W., Koenig, M., and Pines, A., 1990, *Ann. Rev. Phys. Chem.*, **41**, 601; Anandan, J., 1992, *Nature*, **360**, 307; Mead, C. A., 1992, *Rev. mod. Phys.*, **64**, 51.
[2] Moody, J., Shapere, A., and Wilczek, F., 1986, *Phys. Rev. Lett.*, **56**, 893.
[3] Zygelman, B., 1990, *Phys. Rev. Lett.*, **64**, 256.
[4] Bohm, A., Kendrick, B., Loewe, M. E., and Boya, L. J., 1992, *J. math. Phys.*, **33**, 977; Bohm, A., Kendrick, B., and Loewe, M. E., 1992, *Int. J. Quantum Chem.*, **41**, 53.
[5] Steiner, U. E., and Serebrennikov, Yu. A., 1994, *J. chem. Phys.*, **100**, 7503.
[6] Wilczek, F., and Zee, A., 1984, *Phys. Rev. Lett.*, **52**, 2111.
[7] Isham, C. J., 1989, *Modern Differential Geometry for Physicists* (Singapore: World Scientific).
[8] Zee, A., 1988, *Phys. Rev.* **A**, **38**, 1.
[9] Abragam, A., 1961, *The Principles of Nuclear Magnetism* (Oxford: Clarendon Press).
[10] Slichter, C. P., 1978, *Principles of Magnetic Resonance* (Berlin: Springer-Verlag).
[11] Flygare, W. H., 1964, *J. chem. Phys.*, **41**, 793.
[12] Ramsey, N. F., 1950, *Phys. Rev.*, **78**, 699.
[13] Wick, G. C., 1948, *Phys. Rev.*, **73**, 51.
[14] Rigny, P., and Verlet, J., 1967, *J. chem. Phys.*, **47**, 4645.
[15] Serebrennikov, Yu. A., and Steiner, U. E., 1994, *J. chem. Phys.*, **100**, 7508.
[16] Serebrennikov, Yu. A., and Steiner, U. E., 1994, *Chem. Phys. Lett.*, **222**, 309.