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Abstract
Models for three-dimensional macromolecular chains with various angular constrains at thermal equilibrium at room temperature, based on quantum mechanics and a variational procedure, are presented. We get: (i) compact and systematic expressions for the effective quantum kinetic energy Hamiltonian operators (for the unconstrained slowly varying angular degrees of freedom characterizing the macromolecule, responsible for its flexibility), consistently with general requirements, and (ii) effective quantum partition functions. Both (i) and (ii) could, at a later stage, provide further insight or be helpful for specific computations. Open freely rotating chains are studied in detail: the method also yields classical partition functions for them, which imply the existence of persistence lengths consistently. Other macromolecular chains also treated, more succinctly, are: (1) closed-ring freely rotating, (2) open freely rotating with further constraints (helical-like, star-like, . . .), (3) open freely rotating double-stranded.

1. Introduction

Macromolecular chains constitute an attractive research field [1–7]. In generic macromolecular chains, atoms are subjected to effective potentials which, near their minima, can be approximated by harmonic-oscillator-like vibrational potentials. Let a macromolecule be at thermal equilibrium, at absolute temperature T ($\simeq 300$ K), and let k_B be Boltzmann's constant. In many cases, its vibrational degrees of freedom about equilibrium configurations have zero-point energy quanta larger than $k_B T$ [8, 9] and should be treated quantum mechanically [10, 11]. Moreover, they can be represented approximately by ground state wavefunctions and decouple consistently, yielding constant bond lengths and, eventually, bond angles and other angular

constraints. See [12, 13] for the above philosophy for freely jointed macromolecules (without angular constraints) and their consistency with the standard Gaussian model. Here, we shall generalize those ideas when angular constraints exist in flexible macromolecules and obtain reliable effective Hamiltonians and partition functions for them, depending only on the relevant unconstrained (slowly varying) angular degrees of freedom. The contents of this work are as follows. Section 2 deals with the results of the variational computation for open freely rotating macromolecular chains. Further results are given in appendix A. Appendix B discusses the consistency of the effective quantum description. Section 3 outlines results for the other macromolecular chains (1)–(3), as indicated in the abstract. As an application, the classical limit for open freely rotating chains and its physical consistency are treated in section 4. Section 5 contains the conclusions and some discussions.

2. Open freely rotating macromolecular chain

In three-dimensional space, we shall consider a system of N non-relativistic atoms, with masses M_i. Let $\mathbf{R}_i$, $\mathbf{R}_{CM}$ and $\mathbf{y}_i$ $(1 \leqslant i \leqslant N - 1)$ be the position vectors of the atoms, those of the centre of mass (CM) and the relative ones for the atoms, respectively. One has $\mathbf{R}_{CM} = M^{-1} \sum_{i=1}^{N} M_i \mathbf{R}_i$ and $\mathbf{y}_i = \mathbf{R}_{i+1} - \mathbf{R}_i$ $(M = \sum_{i=1}^{N} M_i)$. The quantum Hamiltonian operator is $\tilde{H}_1 + E_{el}$, $\tilde{H}_1 = -\sum_{i=1}^{N} (\hbar^2/2M_i)\nabla_{\mathbf{R}_i}^2 + U$. $\hbar$ is Planck's constant and ∇ is the gradient operator. We are treating the molecular chain in the framework of the Born–Oppenheimer approximation [8], so that the (most rapidly varying) electronic degrees of freedom have already been integrated out and their effect is accounted for by $E_{el} + U$. E_{el} (<0) is the electronic energy (essentially, a constant), which will always be subtracted. U is the remaining (real) atomic potential energy. We get $\tilde{H}_1 = -(\hbar^2/2M)\nabla_{\mathbf{R}_{CM}}^2 + \tilde{H}$, with $(\mathbf{y} \equiv (\mathbf{y}_1, \mathbf{y}_2, \ldots, \mathbf{y}_{N-1}))$:

$$\tilde{H} = -\frac{\hbar^2}{2} \sum_{i,j=1}^{N-1} A_{ij} \nabla_{\mathbf{y}_i} \cdot \nabla_{\mathbf{y}_j} + U(\mathbf{y}). \tag{1}$$

The constants A_{ij} are given by: $M_i^{-1} + M_{i+1}^{-1}$ if $i = j$; $-M_i^{-1}$ if $j = i - 1$ or $j = i + 1$; and 0, otherwise. $U = U(\mathbf{y})$ is independent on $\mathbf{R}_{CM}$. We shall suppose that, approximately, nearest-neighbour atoms interact through harmonic-oscillator-like potentials $V_j = (2A_{jj})^{-1}\omega_{0,j}^2(y_j - d_j)^2$ $(y_j = |\mathbf{y}_j|)$ with vibrational frequencies $\omega_{0,j}$ and bond lengths d_j [12], and that similar potentials exist between atoms which are next-to-nearest neighbours: $V_{j,j+1} = 2^{-1}B_{j,j+1}\omega_{0,j,j+1}^2(|\mathbf{y}_j + \mathbf{y}_{j+1}| - d_{j,j+1})^2$. $\omega_{0,j,j+1}$ are other frequencies, $d_{j,j+1}$ are lengths such that $|d_j - d_{j+1}| \leqslant d_{j,j+1} \leqslant d_j + d_{j+1}$ and $B_{j,j+1}(M_j^{-1} + M_{j+1}^{-1}) = 1$. Then,

$$U(\mathbf{y}) = \sum_{j=1}^{N-1} V_j + \sum_{j=1}^{N-2} V_{j,j+1}. \tag{2}$$

For suitably large $\omega_{0,j,j+1}$, $\sum_{j=1}^{N-2} V_{j,j+1}$ hinders parts of the allowed internal rotations in the macromolecular chain, which becomes a freely rotating one. On physical grounds, $\sum_{j=1}^{N-2} V_{j,j+1}$ could approximate for the effect of the covalent bonding due to successive single pairs of shared electrons, which produce precisely those hindrances [1–3]. In three-dimensional spherical coordinates,

$$- i\hbar\nabla_{\mathbf{y}_i} = -\frac{\mathbf{a}_i}{y_i} - i\hbar\mathbf{u}_{y_i}\frac{\partial}{\partial y_i}, \tag{3}$$

$$\mathbf{y}_i = y_i\mathbf{u}_{y_i}, \qquad \mathbf{a}_i = i\hbar\mathbf{u}_{\theta_i}\frac{\partial}{\partial\theta_i} + i\hbar\mathbf{u}_{\varphi_i}\frac{1}{\sin\theta_i}\frac{\partial}{\partial\varphi_i}, \tag{4}$$

$$\mathbf{u}_{y_i} = (\cos\varphi_i\sin\theta_i, \sin\varphi_i\sin\theta_i, \cos\theta_i), \tag{5}$$

$$\mathbf{u}_{\theta_i} = (\cos \varphi_i \cos \theta_i, \sin \varphi_i \cos \theta_i, -\sin \theta_i), \tag{6}$$

$$\mathbf{u}_{\varphi_i} = (-\sin \varphi_i, \cos \varphi_i, 0). \tag{7}$$

The vectors $\mathbf{u}_{y_i}, \mathbf{u}_{\varphi_i}, \mathbf{u}_{\theta_i}$ constitute an orthonormal set. One has $\prod_{l=1}^{N-1} d^3\mathbf{y}_l = [d\mathbf{y}] = [\prod_{l=1}^{N-1} y_l^2 dy_l][d\Omega]$, with $[d\Omega] \equiv \prod_{l=1}^{N-1} d\varphi_l \, d\theta_l \sin \theta_l$. Let $\theta \equiv (\theta_1, \ldots, \theta_{N-1})$ and $\varphi \equiv (\varphi_1, \ldots, \varphi_{N-1})$. For large N, let the chain be in thermodynamical equilibrium, at $T \simeq 300$ K. The quantum partition function Z for the chain is [14]

$$Z = \text{Tr}[\exp[-(k_B T)^{-1}\tilde{H}]] = \sum_\sigma \exp\left[-\frac{E_\sigma}{k_B T}\right]. \tag{8}$$

Here, Tr represents the trace, σ denotes here the set of all quantum states and E_σ are the eigenvalues of the entire spectrum of the quantum Hamiltonian $\tilde{H}$. The degrees of freedom associated with $\mathbf{R}_{\text{CM}}$ have been factored out. We shall suppose [8, 9]

$$\hbar\omega_{0,l} > k_B T, \qquad \hbar\omega_{0,l} > \frac{\hbar^2 A_{ll}}{d_l^2}, \tag{9}$$

$$\hbar\omega_{0,l,l+1} > k_B T, \qquad \hbar\omega_{0,l,l+1} > \frac{\hbar^2 A_{ll}}{d_l^2}, \tag{10}$$

for any l. Based upon Z and equations (9), (10), the following variational computation will lead to a model for an open freely rotating chain, in which all d_j and $d_{j,j+1}$ are given constants. We choose the variational (radial–angular) wavefunction $\Phi(\mathbf{y})$ as

$$\Phi(\mathbf{y}) = \phi_{\text{nn}}(y)\phi_{\text{nnn}}(\mathbf{y})\psi_\sigma(\theta, \varphi), \tag{11}$$

$$\phi_{\text{nn}}(y) = \prod_{l=1}^{N-1} \phi_l, \qquad \phi_l = d_l^{-1}\left[\frac{\omega_{0,l}}{\pi \hbar A_{ll}}\right]^{1/4} \exp\left[-\frac{\omega_{0,l}}{2\hbar A_{ll}}(y_l - d_l)^2\right]. \tag{12}$$

We choose $\phi_{\text{nnn}}(\mathbf{y}) = \prod_{l=1}^{N-2} \phi_{l,l+1}$. $\phi_{l,l+1}$, associated with $V_{l,l+1}$, is

$$\phi_{l,l+1} = \left[\frac{\omega_{0,l,l+1}B_{l,l+1}}{\pi\hbar}\right]^{1/4} \exp\left[-\frac{\omega_{0,l,l+1}B_{l,l+1}}{2\hbar}(|\mathbf{y}_l + \mathbf{y}_{l+1}| - d_{l,l+1})^2\right]. \tag{13}$$

As all frequencies $\omega_{0,l}$ and $\omega_{0,l,l+1}$ become suitably large, localized Gaussians approach Dirac delta functions ($w_{\text{rad}} = [\prod_{l=1}^{N-1} d_l^{-2}\delta(y_l - d_l)]$):

$$|\phi_{\text{nn}}(y)\phi_{\text{nnn}}(\mathbf{y})|^2 \to w_{\text{rad}}w_{\text{ang}}, \tag{14}$$

$$w_{\text{ang}} = \left[\prod_{l=1}^{N-2} \delta(|d_l\mathbf{u}_{y_l} + d_{l+1}\mathbf{u}_{y_{l+1}}| - d_{l,l+1})\right]. \tag{15}$$

The complex functions $\psi_\sigma(\theta, \varphi)$ (σ now being a set of quantum numbers) are arbitrary, except for some restrictions: (i) they are periodic in each φ_i with period 2π and independent of any y_l; and (ii) they are normalized with respect to the scalar product:

$$(\psi_1, \psi_2) \equiv \int [d\Omega] \, w_{\text{ang}}\psi_1(\theta, \varphi)^*\psi_2(\theta, \varphi). \tag{16}$$

One evaluates, as all frequencies $\omega_{0,i}, i = 1, \ldots, N-1$, and $\omega_{0,l,l+1}, l = 1, \ldots, N-2$, grow large, the quantum expectation value $\langle \Phi, \tilde{H}\Phi \rangle \equiv \int [d\mathbf{y}] \, \Phi(\mathbf{y})^*\tilde{H}\Phi(\mathbf{y})$, by using equations (9)–(16). The computations, which generalize non-trivially those in [15], are very lengthy and will be omitted. For previous (and far simpler) variational calculations, see [13] and references therein. One finds

$$\langle \Phi, \tilde{H}\Phi \rangle = \int [d\Omega] \, \psi_\sigma^*(\theta, \varphi)w_{\text{ang}}E_0\psi_\sigma(\theta, \varphi) + (\psi_\sigma, \tilde{H}_{\text{ang}}\psi_\sigma), \tag{17}$$

$$(\psi_\sigma, \tilde{H}_{\text{ang}}\psi_\sigma) = \int [d\Omega] \, \psi_\sigma^*(\theta, \varphi)w_{\text{ang}}\tilde{H}_{\text{ang}}\psi_\sigma(\theta, \varphi), \tag{18}$$

for any normalized $\psi_\sigma(\theta, \varphi)$ fulfilling the above requirements. Due to certain remarkable exact cancellations, E_0 turns out to be independent of θ, φ and equals the sum of the zero-point energies associated with all V_i and $V_{j,j+1}$: $E_0 = \sum_{i=1}^{N-1} 2^{-1}\hbar\omega_{0,i} + \sum_{i=1}^{N-2} 2^{-1}\hbar\omega_{0,i,i+1}$. In turn, the angular Hamiltonian $\tilde{H}_{ang}$ is

$$w_{ang}\tilde{H}_{ang} = w_{ang}\tilde{H}_{ang,0} + w_{ang}\mathcal{O}_{ang}(\hbar), \tag{19}$$

$$(\psi_1, \tilde{H}_{ang,0}\psi_2) = \int [d\Omega] \frac{1}{2} \sum_{i,j=1}^{N-1} \frac{A_{ij}}{d_i d_j} (\mathbf{e}_i \psi_1(\theta, \varphi))^* w_{ang}(\mathbf{e}_j \psi_2(\theta, \varphi)) \tag{20}$$

with $\mathbf{e}_l \equiv i\hbar\mathbf{u}_{y_l} - \mathbf{a}_l$, $l = 1, \ldots, N-1$. $w_{ang}\mathcal{O}_{ang}(\hbar)$ denotes the set of all remaining contributions which do not depend on any of the frequencies $\omega_{0,i}$ and $\omega_{0,i,i+1}$. $w_{ang}\mathcal{O}_{ang}(\hbar)$ is proportional to $\hbar^2$ and it does not contain differential operators acting upon $\psi_\sigma(\theta, \varphi)$ (that is, $w_{ang}\mathcal{O}_{ang}(\hbar)$ acts multiplicatively on $\psi_\sigma(\theta, \varphi)$). Explicit forms of $w_{ang}\tilde{H}_{ang,0}$ and $w_{ang}\mathcal{O}_{ang}(\hbar)$ are given in appendix A.

Let Φ_σ be an arbitrary orthonormal set of wavefunctions for the system. It is not required that the Φ_σ coincide with the exact eigenfunctions of $\tilde{H}$. Then, the exact Z in equation (8) satisfies Peierls' variational inequality [14]:

$$Z \geqslant \sum_\sigma \exp[-(k_B T)^{-1}\langle \Phi_\sigma, \tilde{H}\Phi_\sigma \rangle], \tag{21}$$

where the equality holds if Φ_σ is the complete set of exact eigenfunctions of $\tilde{H}$. In our case, $\Phi_\sigma = \Phi(\mathbf{y})$ and $\langle \Phi_\sigma, \tilde{H}\Phi_\sigma \rangle$ are given in equations (11) and (17)–(20). Then,

$$Z \geqslant \exp[-(k_B T)^{-1}E_0]Z_{ang}, \tag{22}$$

$$Z_{ang} \equiv \sum_\sigma \exp\left[-(k_B T)^{-1} \int [d\Omega] \psi_\sigma^*(\theta, \varphi) w_{ang}\tilde{H}_{ang}\psi_\sigma(\theta, \varphi)\right]. \tag{23}$$

Z_{ang} can be regarded as the effective three-dimensional quantum partition function for the unconstrained angular degrees of freedom of the freely rotating chain. Some integrations by parts show that $\tilde{H}_{ang,0}$ and $\tilde{H}_{ang}$ are Hermitian operators (with respect to the scalar product in equations (16)). We shall suppose that all angular wavefunctions $\psi_\sigma(\theta, \varphi)$ are the complete set of all orthonormalized eigenfunctions of $\tilde{H}_{ang}$, so that equation (23) becomes $Z_{ang} = \text{Tr}[\exp[-(k_B T)^{-1}\tilde{H}_{ang}]]$. The quantum mechanical description of the chain provided by $\tilde{H}_{ang}$ is physically consistent, as shown in appendix B.

3. Generalizations to other macromolecular chains

We have obtained quantum mechanical models for other three-dimensional macromolecular chains in thermodynamical equilibrium at absolute temperature T, by generalizing the above analysis and variational approach in section 2 and appendices A and B. In all cases, we have shown that the corresponding E_0 is independent of angles and equals the sum of the corresponding zero-point energies. The structures of the resulting effective quantum Hamiltonian and partition function are similar to the ones above for the freely rotating one and will be either omitted or given succinctly.

(1) *Closed-ring freely rotating chain.* Let $\mathbf{y}_N \equiv -\sum_{j=1}^{N-1} \mathbf{y}_j$ and let $y_N = |\mathbf{y}_N|$. Both y_N and $\mathbf{y}_N$ depend on the $2(N-1)$ angles characterizing $\mathbf{y}_j$, $j = 1, \ldots, N-1$. Equation (2) will now be replaced by $U_{cr}(\mathbf{y}) = U(\mathbf{y}) + V_N + V_{1,N} + V_{N-1,N}$, with $V_N = 2^{-1}B_N\omega_{0,N}^2(y_N - d_N)^2$ $(B_N(M_1^{-1} + M_N^{-1}) = 1)$ and $V_{l,N} = 2^{-1}B_{l,N}\omega_{0,l,N}^2(|\mathbf{y}_l + \mathbf{y}_N| - d_{l,N})^2$ $(B_{l,N}(M_l^{-1} + M_N^{-1}) = 1)$ for $l = 1, N-1$. Thus: (i) another harmonic-oscillator-like potential exists between

the first ($i = 1$) and the last ($i = N$) atoms (V_N), (ii) other two harmonic-oscillator-like potentials exist between the first and the ($N-1$)th atoms ($V_{N-1,N}$) and between the second and the Nth atoms ($V_{1,N}$). $\omega_{0,N}$, $\omega_{0,1,N}$ and $\omega_{0,N-1,N}$ are new (also large) frequencies. d_N, $d_{1,N}$ and $d_{N-l,N}$ are other lengths ($|d_l - d_N| \leqslant d_{l,N} \leqslant d_l + d_N$, $l = 1, N-1$). We use the same $\phi_{nn}(y)$ as in equation (11), but $\phi_{nnn}(\mathbf{y})$ also includes $\phi_N \phi_{1,N} \phi_{N-1,N}$. On the other hand, $\phi_N = d_N^{-1}[\omega_{0,N} B_N/\pi\hbar]^{1/4} \exp[-(\omega_{0,N} B_N/2\hbar)(y_N - d_N)^2]$, while $\phi_{l,N} = [\omega_{0,l,N} B_{l,N}/\pi\hbar]^{1/4} \exp[-(\omega_{0,l,N} B_{l,N}/2\hbar)(|\mathbf{y}_l + \mathbf{y}_N| - d_{l,N})^2]$ for $l = 1, N-1$. We get the same $\tilde{H}_{ang,0}$ while $w_{ang} = d_N^{-2}\delta(y_N - d_N)\delta(|d_1\mathbf{u}_{y_1} + d_N\mathbf{u}_{y_N}| - d_{1,N})[\prod_{l=1}^{N-1} \delta(|d_l\mathbf{u}_{y_l} + d_{l+1}\mathbf{u}_{y_{l+1}}| - d_{l,l+1})]$, with $\mathbf{y}_N = y_N\mathbf{u}_{y_N}$. Notice that $\delta(y_N - d_N)$ now makes the macromolecule become a closed ring, while $\delta(|d_1\mathbf{u}_{y_1} + d_N\mathbf{u}_{y_N}| - d_{1,N})$ and $\delta(|d_{N-1}\mathbf{u}_{y_{N-1}} + d_N\mathbf{u}_{y_N}| - d_{N-1,N})$ constrain the angles between $\mathbf{u}_{y_1}$ and $\mathbf{u}_{y_N}$ and between $\mathbf{u}_{y_{N-1}}$ and $\mathbf{u}_{y_N}$, respectively. As a consistency check, we treat a closed-ring freely jointed macromolecular chain, without potentials hindering angles ($U_{cr}(\mathbf{y}) = \sum_{j=1}^{N-1} V_j + V_N$). Now, $w_{ang} = d_N^{-2}\delta(y_N - d_N)$. We have shown here that the effective Hamiltonian for the closed-ring freely jointed chain (given through equations (A.1) and (A.2)) coincides exactly with the lengthier one given as the sum of several contributions in a previous computation [15].

(2) *Open freely rotating chain with further constraints.* In an open freely rotating macromolecular chain, let additional similar potentials exist so that the total potential energy is $U_{fc}(\mathbf{y}) = U(\mathbf{y}) + \sum_{n(\geqslant 3)} \sum_{i(\geqslant 1)} u_{i-1;i-1+n}$. $U(\mathbf{y})$ is given in equation (2), while $u_{i-1;i-1+n} = 2^{-1} B_{i-1;i-1+n} \omega_{0,i-1;i-1+n}^2 (|\sum_{j=0}^{n-1} \mathbf{y}_{i-1+j}| - d_{i-1;i-1+n})^2$. $\omega_{0,i-1;i-1+n}$ are large frequencies, $d_{i-1;i-1+n}$ are lengths and $B_{i-1;i-1+n}(M_{i-1}^{-1} + M_{i-1+n}^{-1}) = 1$. The sums over n and i involve only some subset of atoms, so the chain still has a large number λN ($0 < \lambda < 1$) of unconstrained angles and, so, it has some flexibility. We now have $w_{ang} = [\prod_{l=1}^{N-2} \delta(|d_l\mathbf{u}_{y_l} + d_{l+1}\mathbf{u}_{y_{l+1}}| - d_{l,l+1})][\prod_n \prod_i \delta(|\sum_{j=0}^{n-1} d_{i-1+j}\mathbf{u}_{y_{i-1+j}}| - d_{i-1;i-1+n})]$. The new potentials u could approximate the covalent bonding between some pairs of atoms, due to double pairs of shared electrons (even in resonance cases) [1–3]. These choices could model hydrogen bonds or the case of a 'helix'.

We have also treated star polymers (SP). We treat the case of n arms ($n \geqslant 3$), all of which start from a certain atom ('the vertex or origin of the star'), with position vector $\mathbf{R}_0$ and mass M_0. The rth arm has N_r atoms (without counting the 'vertex'), forming a linear subchain ($1 \leqslant r \leqslant n$). The mass and the position vector of the ith atom along the rth arm are $M_i^{(r)}$ and $\mathbf{R}_i^{(r)}$ ($1 \leqslant i \leqslant N_r$). The centre-of-mass (CM) position vector and the relative ('bond') ones along the rth arm are $\mathbf{R}_{CM}$ and $\mathbf{y}_i^{(r)}$ ($1 \leqslant i \leqslant N_r$): $\mathbf{R}_{CM} = [M_0\mathbf{R}_0 + \sum_{r=1}^{n} \sum_{i=1}^{N_r} M_i^{(r)}\mathbf{R}_i^{(r)}]/M$ and $\mathbf{y}_i^{(r)} = \mathbf{R}_i^{(r)} - \mathbf{R}_{i-1}^{(r)}$ ($M = M_0 + \sum_{r=1}^{n} \sum_{i=1}^{N_r} M_i^{(r)}$ and $\mathbf{R}_0^{(r)} \equiv \mathbf{R}_0$). Below, let $(\mathbf{y}_1^{(1)}, \ldots) \equiv \mathbf{y}$. The SP potential energy $U(\mathbf{y})_{SP}$ equals the sum of those for all arms (each of them similar to that in equation (2)), plus all those between the first atom in the rth arm and the vertex, plus all those constraining the bond angles between all $\mathbf{y}_1^{(r)}$ and $\mathbf{y}_2^{(r)}$ and between all pairs $\mathbf{y}_1^{(r)}$ and $\mathbf{y}_1^{(r')}$ ($r \neq r$). After separating $\mathbf{R}_{CM}$, equation (1) is replaced by $K_{kin,SP} + U_{SP}$, $K_{kin,SP} = -(\hbar^2/2) \sum_{i,j=1}^{N-1} \sum_{r,r'=1}^{N-1} A_{ij}^{r,r'} \nabla_{\mathbf{y}_i^{(r)}} \nabla_{\mathbf{y}_j^{(r')}}$ being equal to

$$-\frac{\hbar^2}{2M_0}\left[\sum_{r=1}^{n} \nabla_{\mathbf{y}_1^{(r)}}\right]^2 - \sum_{r=1}^{n} \sum_{i=1}^{N_r} \frac{\hbar^2}{2M_i^{(r)}}(\nabla_{\mathbf{y}_i^{(r)}} - \nabla_{\mathbf{y}_{i+1}^{(r)}})^2 \tag{24}$$

and $\nabla_{\mathbf{y}_{N_r+1}^r} \equiv 0$. Equation (A.1) holds, its right-hand side now being $\sum_{i,j=1}^{N-1} \sum_{r,r'=1}^{N-1} (2d_i^{(r)} d_j^{(r')})^{-1} A_{ij}^{r,r'} [\mathbf{e}_i^{(r)}(w_{ang}\mathbf{e}_j^{(r')})]$. w_{ang} equals the product of those for

all arms (each of them similar to that in section 2) times all those constraining the bond angles between all $\mathbf{y}_1^{(r)}$ and $\mathbf{y}_2^{(r)}$ and between all pairs $\mathbf{y}_1^{(r)}$ and $\mathbf{y}_1^{(r')}$ ($r \neq r'$).

(3) *Open freely rotating double-stranded chain.* A previous quantum model for an open freely jointed double-stranded macromolecular chain, given in [12], has now been generalized to one for an open freely rotating double-stranded chain. An attractive total potential energy U_{ds} among atoms belonging to different strands, responsible for the existence of the double strand as a bound state, is included. Let $\mathbf{z}$ denote the relative position vector between the two centres of mass of the two single chains. We now start from equations (50)–(54) in [12], provided that we also include, for each single chain, a suitable $\sum_{j=1}^{N-2} V_{j,j+1}$ and a factor ϕ_{nnn} in the variational wavefunction. Let all frequencies be larger than $(k_B T)/\hbar$ but still not so large as to produce an appreciable break-up or dissociation of the double-stranded chain into two separated single chains. Then, Peierls' inequality also yields an effective quantum partition function for the freely rotating double-stranded (ds) chain as $\exp[-(k_B T)^{-1} E_0] \operatorname{Tr}[\exp[-(k_B T)^{-1} \tilde{H}_{Q,ds,ang}]]$. The quantum Hamiltonian is $w_{ds,ang} \tilde{H}_{ds,ang} = w_{ds,ang}[-(\hbar^2/2M_{red})(\nabla_{\mathbf{z}})^2 + U_{ds} + \sum_{r=1}^{2} \tilde{H}_{ang,0}^{(r)} + \mathcal{O}_{ds,ang}(\hbar)]$. $w_{ds,ang}$ is the product of two terms, each of them like that in equation (15).

4. Open freely rotating chain: simpler Hamiltonian and classical limit

The variational states Φ in equation (11) are genuinely quantum mechanical (see the end of appendix B). In spite of this, it will be possible to proceed to the classical ($\hbar \to 0$) limit, as we shall see. Starting from equations (19) and (20) for the freely rotating chain, we shall perform a further variational computation, in order to arrive at a more manageable effective Hamiltonian, in terms of which the transition to the classical limit can be carried out directly. Before undertaking this, we shall express the $2(N-1)$ angular variables in θ and φ in terms of another set of $2(N-1)$ more suitable ones. The latter will be chosen to be $\theta_1, \ldots, \theta_{N-1}$, φ_0 ($\equiv (N-1)^{-1} \sum_{j=1}^{N-1} \varphi_j$) and $\beta_{j,j+1} \equiv \mathbf{u}_{y_j} \mathbf{u}_{y_{j+1}}$ ($= \cos\theta_j \cos\theta_{j+1} + \sin\theta_j \sin\theta_j \cos(\varphi_{j+1} - \varphi_j)$), $j = 1, \ldots, N-2$. One has: $[\mathrm{d}\Omega] = [\prod_{j=1}^{N-2} \mathrm{d}\beta_{j,j+1}] \mathrm{d}\varphi_0 [\prod_{l=1}^{N-1} \mathrm{d}\theta_l] J$, the Jacobian J depending on all θ_j and $\beta_{j,j+1}$. The angular constraint now becomes $((\mathbf{u}_{y_j} \mathbf{u}_{y_{j+1}})^{(0)} = (2d_j d_{j+1})^{-1}(d_{j,j+1}^2 - d_j^2 - d_{j+1}^2))$

$$w_{ang} = \left[\prod_{j=1}^{N-2} \frac{d_{j,j+1}}{d_j d_{j+1}}\right]\left[\prod_{j=1}^{N-2} \delta(\beta_{j,j+1} - (\mathbf{u}_{y_j} \mathbf{u}_{y_{j+1}})^{(0)})\right]. \tag{25}$$

In the further variational computation, we shall consider restricted angular wavefunctions $\psi_\sigma \equiv \psi_{res;\sigma} = \psi_{res;\sigma}(\theta, \varphi_0)$ which are independent of any $\beta_{j,j+1}$, $j = 1, \ldots, N-2$. On the other hand, $\psi_{res;\sigma}$ is an arbitrary function of $\theta_1, \ldots, \theta_{N-1}$ and φ_0, which is periodic in φ_0 with period 2π, and is normalized with respect to the scalar product in equation (16). We shall define a restricted effective angular Hamiltonian $\tilde{H}_{ang,res}$ (acting only upon the restricted wavefunctions $\psi_{res;\sigma}$) through $(\psi_{res;1}, \tilde{H}_{ang} \psi_{res;2}) = (\psi_{res;1}, \tilde{H}_{ang,res} \psi_{res;2})$. $\tilde{H}_{ang,res}$ is also Hermitian and we choose the $\psi_{res;\sigma}$ to be the complete set of its (orthonormalized) eigenfunctions. Another application of Peierls' inequality (21) to equation (23) gives

$$Z_{ang} \geqslant \operatorname{Tr} \exp[-(k_B T)^{-1} \tilde{H}_{ang,res}] \equiv Z_{ang,res}. \tag{26}$$

Coming back to equation (26), we perform all integrals associated with $[\prod_{j=1}^{N-2} \mathrm{d}\beta_{j,j+1}]$ in $(\psi_{res;1}, \tilde{H}_{ang,res} \psi_{res;2})$, by using all delta functions contained in w_{ang}. Then, the resulting equation (26) has an adequate form for performing the $\hbar \to 0$ limit, under additional assumptions. In agreement with (9) and (10), around room temperature the individual slowly

varying internal rotations about bonds (unconstrained in freely rotating macromolecular chains) have typical energies about two orders of magnitude smaller than the vibrational energies $\hbar\omega_{0,i}$ and $\hbar\omega_{0,l,l+1}$ [2, 8, 9]. Also, let $k_B T > (\hbar^2 A_{ll})/(d_l^2)$, so that an appreciable number of excited states for those unconstrained rotations are occupied and quantum operators and statistics can be approximated by classical ones. All quantities of order $\hbar$ or higher (such as $w_{\mathrm{ang}}\mathcal{O}_{\mathrm{ang}}(\hbar)$) can be neglected. Then, the Hamiltonian $\tilde{H}_{\mathrm{ang,res}}$ becomes, in the classical (C) limit,

$$\tilde{H}_{\mathrm{C,ang,res}} = 2^{-1} \sum_{i,j=1}^{N-1} (d_i d_j)^{-1} A_{ij} \mathbf{a}_{\mathrm{C,res};i} \cdot \mathbf{a}_{\mathrm{C,res};j}. \tag{27}$$

The $\mathbf{a}_{\mathrm{C,res};i}$ are classical variables (arising from the classical limit of $-\mathbf{e}_i$): $\mathbf{a}_{\mathrm{C,res};i} = -[\mathbf{u}_{\theta_i} P_{\theta_i} + ((N-1)\sin\theta_i)^{-1}\mathbf{u}_{\varphi_i} P_{\varphi_0}]$. P_{θ_i} and P_{φ_0} are the classical momenta canonically conjugate to θ_i, $i = 1, \ldots, N-1$, and φ_0. In the classical limit, $Z_{\mathrm{ang,res}}$ becomes the corresponding classical partition function $Z_{\mathrm{C,ang,res}}$. One performs all Gaussian integrations in $Z_{\mathrm{C,ang,res}}$ over the classical momenta P_{θ_i} and P_{φ_0}. Then,

$$Z_{\mathrm{C,ang,res}} = \frac{1}{(2\pi\hbar)^N} 2\pi [2\pi k_B T]^{N/2} \int \left[\prod_{l=1}^{N-1} d\theta_l\right] [D_N]^{-1/2}. \tag{28}$$

D_N is the $N \times N$ symmetric matrix formed by the coefficients of P_{φ_0} and P_{θ_i}, $i = 1, \ldots, N-1$, in $\tilde{H}_{\mathrm{C,ang,res}}$. Previously, a rather different variational computation for freely rotating macromolecular chains [13] has provided a different total zero-point energy (E_0', dependent on all $(\mathbf{u}_{y_j}\mathbf{u}_{y_{j+1}})^{(0)}$), restricted effective quantum angular Hamiltonian ($\tilde{H}_{\mathrm{ang,res}}'$) and quantum partition function $Z_{\mathrm{ang,res}}'$. A new result here is that, even if $E_0' \neq E_0$, the above $\tilde{H}_{\mathrm{C,ang,res}}$ and $Z_{\mathrm{C,ang,res}}$ coincide with the classical limits $\tilde{H}_{\mathrm{C,ang,res}}'$ and $Z_{\mathrm{C,ang,res}}'$ of $\tilde{H}_{\mathrm{ang,res}}'$ and $Z_{\mathrm{ang,res}}'$, respectively. Let $d_j = d$, $j = 1, \ldots, N-1$, and $M_i = M_0$, $i = 1, \ldots, N$. Equation (28) (which may be useful in numerical computations) implies, on the basis of [13] and some long-distance approximations, the existence of a persistence length d_{pl} $(>d)$. So, on a suitably large length scale, the classical freely rotating chain described by equation (27) can be approximated by a freely jointed one having N_{pl} bonds ($N_{\mathrm{pl}} < N-1$) and a new bond length d_{pl}, with overall rotational invariance. Consider many classical freely rotating chains (of identical or different kinds) in thermal equilibrium at T: chemical reactions may take place among pairs of chains, to give other pairs of chains. Through standard studies of chemical reactions [9], the explicit dependence on T of the equilibrium constant for those reactions follows from those in equation (28) (for the partition function of each reacting freely rotating chain); similar conclusions hold if star polymers are involved.

5. Conclusions and critical discussion; the role of excitations

Effective quantum Hamiltonians and partition functions at $T \simeq 300$ K, in terms of unconstrained (slowly varying) angular variables, have been obtained for the following macromolecular chains: open freely rotating, and (1) closed-ring freely rotating, (2) open freely rotating with further constraints, (3) open freely rotating double-stranded. Physical and mathematical structures related to the Born–Oppenheimer approximation have been displayed, which may yield further insight. Our variational computations are non-trivial generalizations of those leading to the Heisenberg–Dirac Hamiltonian describing spin–spin interactions of atoms in magnetic materials [16]. Additional (residual) potential energies U_{res}, depending on the still unconstrained angular degrees of freedom, can be taken into account through $\exp[-(k_B T)^{-1} U_{\mathrm{res}}]$ in the effective partition functions, which may provide a basis for further

(analytical or numerical) computations. It also seems possible to study approximately some excitations of the effective Hamiltonians (at least, in some simplified cases); this lies beyond our scope here.

We shall also discuss briefly the role of excited vibrational states. We start with an open freely jointed chain, so that: (i) $U(\mathbf{y}) = \sum_{j=1}^{N-1} V_j$ in equation (2); (ii) $\Phi(\mathbf{y})_1 = \phi_{nn,1}(y)\psi_\sigma(\theta, \varphi)$; (iii) $\phi_{nn,1}(y) = \prod_{l=1}^{N-1} \phi_{l,n(l)}$, $\phi_{l,n(l)}$ $(n(l) = 0, 1, 2, \ldots, n(l, \max))$ being, essentially, the $n(l)$th eigenfunction of V_j, for suitably large $\omega_{0,l}$ [12]. The V_j are physically reliable here as long as we include only a reasonable subset formed by its lower eigenfunctions, with finite $n(l, \max) < +\infty$. Then, one continues to apply Peierls' inequality, Φ_σ now being all the above $\Phi(\mathbf{y})_1$. For $\hbar\omega_{0,l} > k_B T$, one finds equations (17), (18) and (22) with $w_{\mathrm{ang}} \equiv 1$ and $\exp[-(k_B T)^{-1} E_0]$ replaced by $Z_{\mathrm{vibr}} = \exp[-(k_B T)^{-1} E_0 + \sum_{l=1}^{N-1} \ln[1 - \exp(-(n(l, \max) + 1)(\hbar\omega_{0,l}/k_B T))]/[1 - \exp(-(\hbar\omega_{0,l}/k_B T))]]$. For $n(l, \max)$ not large, Z_{vibr} is better approximated by $\exp[-(k_B T)^{-1} E_0]$ and the contributions of excited vibrational states and of superpositions thereof (approximating collective excitations along the chain—say, longitudinal) become more negligible as all $\hbar\omega_{0,l}/(k_B T)$ become larger, in qualitative agreement with [10] and [11]. Similar conclusions seem to hold, on a suitably large length scale, for a freely rotating chain: recall that the latter can be approximated, on such a scale, by a freely jointed one having N_{pl} bonds and a new bond length d_{pl}. Similar statements may hold (for suitable large length scales) for other chains provided that they have a number of unconstrained angular degrees of freedom proportional to N. Finally, we turn to an open long macromolecular chain such that every atom oscillates about some position $\mathbf{R}_i^{(0)}$ fixed in the macromolecule, $n(l, \max)$ being not small and all frequencies being $\leqslant \hbar^{-1} k_B T$ and not much larger than $\hbar^2 A_{ll}/d_l^2$. Overall rotations of the whole macromolecule are disregarded in what follows. Then, a possible approximation consists in replacing the actual total potential $U(\mathbf{y})$ by a sum, $U_{\mathrm{ahp}}(\mathbf{y})$, of approximate harmonic potentials, analogous to those for crystals, although the $\mathbf{R}_i^{(0)}$ are not distributed with strict periodicity. As N is large, some, at least, of the vibrational normal modes described by $U_{\mathrm{ahp}}(\mathbf{y})$ about those fixed positions may resemble, more or less, collective excitations propagating along the chain with different frequencies ω_α (α being indices or parameters which distinguish different modes), in qualitative agreement with [16, 17]. Those excitations can be classified roughly as 'acoustic' or 'optical', depending on whether ω_α can become appreciably smaller than $\hbar^{-1} k_B T$ or not. 'Optical' excitations (with frequencies that are $\simeq \hbar^{-1} k_B T$) may play a role similar to the vibrations of an open freely jointed chain, discussed above. Peierls' inequality (for the quantum partition function determined by $U(\mathbf{y})$ or $U_{\mathrm{ahp}}(\mathbf{y})$) retaining only more or less localized Φ_σ having frequencies that are $\simeq \hbar^{-1} k_B T$ would lose accuracy, and would not suffice for yielding reasonable approximations, due to the 'acoustic' excitations with $\hbar\omega_\alpha < k_B T$. On the other hand, one could approximate the quantum description of those 'acoustic' vibrational excitations with suitably small frequency ($\hbar\omega_\alpha < k_B T$) by a classical one [9, 16].

Acknowledgments

Appendix A. Expressions for $\tilde{H}_{\mathrm{ang},0}$ and $\mathcal{O}_{\mathrm{ang}}$

$$w_{\mathrm{ang}}\tilde{H}_{\mathrm{ang},0} = \frac{1}{2}\sum_{i,j=1}^{N-1}\frac{A_{ij}}{d_i d_j}[\mathbf{e}_i \cdot (w_{\mathrm{ang}}\mathbf{e}_j)], \tag{A.1}$$

$$w_{\text{ang}}\mathcal{O}_{\text{ang}}(\hbar) = \frac{1}{2}\sum_{i=1}^{N-1}\left[-\frac{\hbar^2 A_{ii}}{d_i^2}w_{\text{ang}} + \frac{A_{ii}}{2}(-i\hbar\nabla_{\mathbf{y}_i})^2 w_{\text{ang},1}\right]$$

$$-\sum_{i=1}^{N-1}\frac{1}{2M_i}\left[(-i\hbar\nabla_{\mathbf{y}_{i-1}})\cdot(-i\hbar\nabla_{\mathbf{y}_i}) + \frac{1}{2}(-i\hbar\nabla_{\mathbf{y}_{i-1}})\cdot\left(i\hbar\mathbf{u}_{y_i}\frac{\partial}{\partial y_i}\right)\right.$$

$$\left.+\frac{1}{2}(-i\hbar\nabla_{\mathbf{y}_i})\cdot\left(i\hbar\mathbf{u}_{y_{i-1}}\frac{\partial}{\partial y_{i-1}}\right) + \frac{1}{2}\left(i\hbar\mathbf{u}_{y_i}\frac{\partial}{\partial y_i}\right)\cdot\left(i\hbar\mathbf{u}_{y_{i-1}}\frac{\partial}{\partial y_{i-1}}\right)\right]w_{\text{ang},1}.$$

$$\text{(A.2)}$$

So, $w_{\text{ang}}\mathcal{O}_{\text{ang}}(\hbar)$ contains first and second derivatives of $w_{\text{ang},1} \equiv [\prod_{l=1}^{N-2}\delta(|\mathbf{y}_l+\mathbf{y}_{l+1}|-d_{l,l+1})]$. It is understood that in equation (A.2), after having differentiated with respect to all y_l, one sets $y_l = d_l$ for $l = 1,\ldots,N-1$. In order to define $\tilde{H}_{\text{ang},0}$, it seems that one should divide the right-hand side of equation (A.1) by w_{ang} which, in turn, would lead to mathematically unpleasant expressions such as $w_{\text{ang}}^{-1}[\mathbf{a}_l w_{\text{ang}}]$. Fortunately, notice that we also define $\tilde{H}_{\text{ang},0}$ through equation (20), for the generic functions ψ_1, ψ_2 appearing in equation (16) (and making all integrals converge). In the integral yielding $(\psi_1, \tilde{H}_{\text{ang},0}\psi_2)$, the expression $w_{\text{ang}}^{-1}[\mathbf{a}_l w_{\text{ang}}]$ does not appear, so our procedure is mathematically correct. Upon performing algebraic manipulations, it will be economical (in particular, in appendix B) to work with expressions in which w_{ang}^{-1} times some angular derivative of w_{ang} appears eventually. Such formal expressions receive mathematical support from performing integrations in the scalar product in equation (16).

Appendix B. Probability conservation and overall rotational invariance

Let the freely rotating macromolecular chain be, at time t, in a pure state $\psi = \psi(\theta, \varphi; t)$. Then, the latter evolves slowly through the Schrödinger equation: $w_{\text{ang}}\tilde{H}_{\text{ang}}\psi = i\hbar w_{\text{ang}}(\partial\psi/\partial t)$. This yields the continuity equation

$$\frac{1}{2i\hbar}\sum_{i,j=1}^{N-1}\frac{1}{\sin\theta_i}\frac{A_{ij}}{d_i d_j}\mathbf{a}_{\text{ad};i}[\sin\theta_i w_{\text{ang}}\cdot(\psi^*\mathbf{a}_j\psi - \psi\mathbf{a}_j\psi^*)] = \frac{\partial[w_{\text{ang}}\psi^*\psi]}{\partial t}. \tag{B.1}$$

In turn, $\mathbf{a}_{\text{ad};i}$ acting upon an arbitrary $f = f(\theta, \varphi; t)$ is defined as $\mathbf{a}_{\text{ad};i}f = i\hbar(\partial(f\mathbf{u}_{\theta_i})/\partial\theta_i) + (i\hbar/\sin\theta_i)(\partial(f\mathbf{u}_{\varphi_i})/\partial\varphi_i)$. Equation (B.1) implies total probability conservation consistently: $\partial(\int[d\Omega]\,w_{\text{ang}}\psi^*\psi)/\partial t = 0$.

The fact that $\tilde{H}_{\text{ang},0}$ is given in terms of $\mathbf{e}_j$ appears to suggest that the latter operators could play an important role. Since, according to (16), $(\psi_1, \mathbf{e}_j\psi_2) = \int[d\Omega]\,\psi_1^*(\theta, \varphi)w_{\text{ang}}\mathbf{e}_j\psi_2(\theta, \varphi)$, it turns out that $(\psi_1, \mathbf{e}_j\psi_2) \neq (\mathbf{e}_j\psi_1, \psi_2)$; that is, $\mathbf{e}_j$ is not Hermitian. However, the new quantum variables $\mathbf{e}_{h;j}$ defined through $w_{\text{ang}}\mathbf{e}_{h;j} \equiv w_{\text{ang}}\mathbf{e}_j - 2^{-1}\mathbf{a}_j w_{\text{ang}}$ are Hermitian (h) operators as regards equations (16). The quantum variables $\mathbf{e}_{h;j}$, which could be regarded as some sort of transverse momenta for the actual freely rotating chain, have certain interesting properties. In order to display them, the orbital angular momenta for the jth bond, $\mathbf{l}_j = \mathbf{y}_j \times (-i\hbar)\nabla_{\mathbf{y}_j}$, have also to enter into the game. $\mathbf{l}_j$ is not Hermitian in the scalar product (16) either. However, the new operator $\mathbf{l}_{h;j}$ such that $w_{\text{ang}}\mathbf{l}_{h;j} \equiv w_{\text{ang}}\mathbf{l}_j + 2^{-1}\mathbf{l}_j w_{\text{ang}}$ is Hermitian with respect to equations (16). Then, $\mathbf{L}_h = \sum_{j=1}^{N-1}\mathbf{l}_{h;j}$ is the total orbital angular momentum operator, which is also Hermitian. An important question of principle is whether the actual (Hermitian) Hamiltonian $\tilde{H}_{\text{ang}}$ is invariant under overall rotations—that is, whether $\tilde{H}_{\text{ang}}$ commutes with the total orbital angular momentum $\mathbf{L}_h$. In order to answer that question, we shall need some useful algebraic

relations. Let $e_{h;j,\alpha}$ and $l_{h;j,\alpha}$, $\alpha = 1, 2, 3$, be the cartesian components of $\mathbf{e}_{h;j}$ and $\mathbf{l}_{h;j}$, respectively ($j = 1, \ldots, N-1$). Some algebra yields the following commutation relations ($[A, B] = AB - BA$): $[e_{h;k,\alpha}, e_{h;j,\beta}] = -i\hbar\delta_{k,j}\epsilon_{\alpha\beta\gamma}l_{h;j,\gamma}$, $[l_{h;k,\alpha}, e_{h;j,\beta}] = i\hbar\delta_{k,j}\epsilon_{\alpha\beta\gamma}e_{h;j,\gamma}$ and $[l_{h;k,\alpha}, l_{h;j,\beta}] = i\hbar\delta_{k,j}\epsilon_{\alpha\beta\gamma}l_{h;j,\gamma}$. $\delta_{k,j}$ and $\epsilon_{\alpha\beta\gamma}$ are, respectively, the Kronecker delta and the totally antisymmetric tensor with three indices ($\epsilon_{123} = +1$ etc). On the other hand, for any function f which depends solely on scalar products of the various vectors $\mathbf{u}_{y_l}$ among themselves (or only on scalar products of the vectors $\mathbf{y}_l$ among themselves), but not on $\mathbf{u}_{\varphi_l}, \mathbf{u}_{\theta_l}$, one has [8] $\sum_{j=1}^{N-1} \mathbf{l}_j f = 0$. Consequently $\sum_{j=1}^{N-1} \mathbf{l}_j w_{\text{ang}} = 0$ and, hence, $\mathbf{L}_h = \sum_{j=1}^{N-1} \mathbf{l}_j$, $\mathbf{L}_h w_{\text{ang}} = 0$ and $\mathbf{L}_h w_{\text{ang},1} = 0$. Using the above commutation relations, one finds $[\tilde{H}_{\text{ang},0}, \mathbf{L}_h] = 0$. Finally, we recall the expression for $\mathcal{O}_{\text{ang}}(\hbar)$ in equation (A.2). We realize that, in the latter equation, the various operators acting upon $w_{\text{ang},1}$ are expressed as scalar products of the $-i\hbar\nabla_{\mathbf{y}_i}$ among themselves, of $-i\hbar\nabla_{\mathbf{y}_i}$ with $i\hbar\mathbf{u}_{y_j}\frac{\partial}{\partial y_j}$, with $j = i \pm 1$, and of $i\hbar\mathbf{u}_{y_j}\frac{\partial}{\partial y_j}$ with $i\hbar\mathbf{u}_{y_j}\frac{\partial}{\partial y_i}$ ($j = i \pm 1$). All such scalar products commute with $\sum_{j=1}^{N-1} \mathbf{l}_j$. Then, one readily finds $[\mathcal{O}_{\text{ang}}(\hbar), \mathbf{L}_h] = 0$. Consequently, $\tilde{H}_{\text{ang}}$ is invariant under overall rotations: $[\tilde{H}_{\text{ang}}, \mathbf{L}_h] = 0$.

It is easy to see that the quantum uncertainty of $\mathbf{e}_{h,j,\alpha}$ in ψ_σ (a generic normalized eigenfunction of $\tilde{H}_{\text{ang}}$) develops contributions linear in $\hbar\omega_{0,l,l+1}$.

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