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Elongation 法を用いた電子スペクトル計算のためのMD法

（九大院・総理工 [1]，JST-CREST[2]）○Pomogaev Vladimir[1], Pomogaeva Anna[1], Gu FengLong[1],

青木 百合子 [1,2]

Photophysical properties of polyethylene structures embedding aromatic fragments (benzene, anthracene, DCM, tryptophan, and estradiol) responsible for existence lowest electronically exited states were studied by new technique involving the elongation method applied to quantum-chemical calculations. Absorption spectra, energetic vertical scheme, and some photophysical properties were obtained. The comparison between the elongation and the conventional calculations was made, and it is shown that the elongation method is a powerful tool to determine the excited states, as well as optical properties for large systems. Also, the work concerned absorption spectrum of tryptophan cage mini-protein under thermo-dynamical conditions in a molecular dynamic (MD) cell by using a hybrid of the elongation and Configuration Interaction Singles (CIS) methods (MD-CIS-elongation).

The main idea of elongation method is to extend a polymer structure by adding a monomer unit stepwise to a starting oligomer while keeping the variational degrees of freedom fixed. MOs of a starting cluster are divided into 'frozen' (FLMO) and 'active' (ALMO) regionally localized MO (RLMO). Simultaneously the total AO basis is divided on A (frozen AOs) and B (active AOs) regions. An attacking monomer is jointed to the active region, and the new Fock-matrix formed on base of ALMO.[1]

$$|i\rangle_{RLMO}^{CMO} = \sum_m \left(C_{RLMO}^{CMO} \right)_{im} \phi_m \quad \text{where RLMO basis is} \quad \phi_m = \sum_\mu \left(C_{AO}^{RLMO} \right)_{m\mu} \chi_\mu. \tag{1}$$

The advantage of the elongation method for calculating MOs is that the frozen regions being far away from the interactive site are excluded from the elongation SCF procedure.

Energies E_p of exited states can be found by applying CIS from the secular equation

$$\sum_{(jl')} A_{jl',p} \left(H_{ik',jl'} - E_p \right) = 0 \tag{2}$$

where $\quad H_{ik',jl'} = \left\langle \Phi_{ik'} \left| H \right| \Phi_{jl'} \right\rangle = \delta_{ij} \delta_{kl'} \left(\varepsilon_{k'} - \varepsilon_i \right) - \langle ij | k'l' \rangle + 2\delta_\lambda \langle ik' | jl' \rangle \tag{3}$

calculated in the framework of INDO with coulombic $\gamma_{\mu\nu}$ and exchange $\tilde{\gamma}_{\mu\nu}$ integrals through

$$\langle ij | k'l' \rangle = \sum_\mu c_{i\mu} c_{j\mu} c_{k'\mu} c_{l'\mu} \gamma_{\mu\mu} + \sum_{\mu<\nu} \left[\left(c_{i\mu} c_{j\mu} c_{k'\nu} c_{l'\nu} + c_{i\nu} c_{j\nu} c_{k'\mu} c_{l'\mu} \right) \gamma_{\mu\nu} + \left(c_{i\mu} c_{j\nu} + c_{i\nu} c_{j\mu} \right) \left(c_{k'\mu} c_{l'\nu} + c_{k'\nu} c_{l'\mu} \right) \tilde{\gamma}_{\mu\nu} \right], \tag{4a}$$

$$\langle ik' | jl' \rangle = \sum_\mu c_{i\mu} c_{j\mu} c_{k'\mu} c_{l'\mu} \gamma_{\mu\mu} + \sum_{\mu<\nu} \left[\left(c_{i\mu} c_{k'\mu} c_{j\nu} c_{l'\nu} + c_{i\nu} c_{k'\nu} c_{j\mu} c_{l'\mu} \right) \gamma_{\mu\nu} + \left(c_{i\mu} c_{k'\nu} + c_{i\nu} c_{k'\mu} \right) \left(c_{j\mu} c_{l'\nu} + c_{j\nu} c_{l'\mu} \right) \tilde{\gamma}_{\mu\nu} \right]. \tag{4b}$$

Several ways might be considered to apply CIS treatment with the elongation method.[2] One of them 'direct or conventional CIS (CCIS)' can be considered after all elongation steps finished. The approach allows the Fock matrix of the total system to be diagonalized in RLMO basis and then, CMOs are

obtained by returning into AO basis. The total RLMOs $\mathbf{C}_{AO}^{RLMO}(\Sigma)$ can be constructed from $\mathbf{C}_{AO}^{RLMO}(R_g)$ of each gth region as

$$\mathbf{C}_{AO}^{RLMO}(\Sigma)=\mathbf{C}_{AO}^{RLMO}(R_1)\cup...\cup\mathbf{C}_{AO}^{RLMO}(R_g)\cup...\cup\mathbf{C}_{AO}^{RLMO}(R_{last}), \quad \mathbf{F}_{RLMO}=\mathbf{C}_{AO}^{RLMO+}(\Sigma)\mathbf{F}_{AO}\mathbf{C}_{AO}^{RLMO}(\Sigma). \quad (5)$$

It should be mentioned that if only some special regions are concerned, the total RLMOs can be constructed by the RLMOs from these regions for CCIS calculation. This method allows matrix elements of CIS (Eq. 3) to be collected from selected RLMOs instead the total basis that can reduce dimension of the matrix for many types of compounds. The new definition maintains the forms of Eqs. 4 but the MO coefficients are replaced by $c \equiv \tilde{C}_{AO}^{CMO}$. Then, another "truncated basis" approach can be applied. Summations over AOs μ and ν (Eqs. 4) are shorted when all values of MO coefficients for the selected orbitals i, j, k', l' are less than 10^{-2} that leads to the accuracy of a product between four coefficients better than 10^{-8}.

MD can be involved also for obtaining vibrational modes to define the profile and width of absorption or emission spectra. An ensemble of chromophores and surrounding molecules under thermo-dynamical impact could reproduce vibronic processes. Absorption or emission spectral width is divided into $\Delta\lambda$ wave-length intervals interpreted as "frequency resolution". The averaged absorption band $\Delta\lambda$ efficacy is defined through the relative molar coefficient $\varepsilon(\Delta\lambda) = p_{\Delta\lambda}f$ and a relative radiation intensity is $I_{\Delta\lambda} = p_{\Delta\lambda}\cdot k_r\cdot\Phi$ where $p_{\Delta\lambda} = N_{\Delta\lambda}/N$ is probability to find transition in conformer on this $\Delta\lambda$ interval. The averaged oscillator strength f, radiative rate constant k_r, and fluorescent quantum yield Φ are defined also on this energy gap.
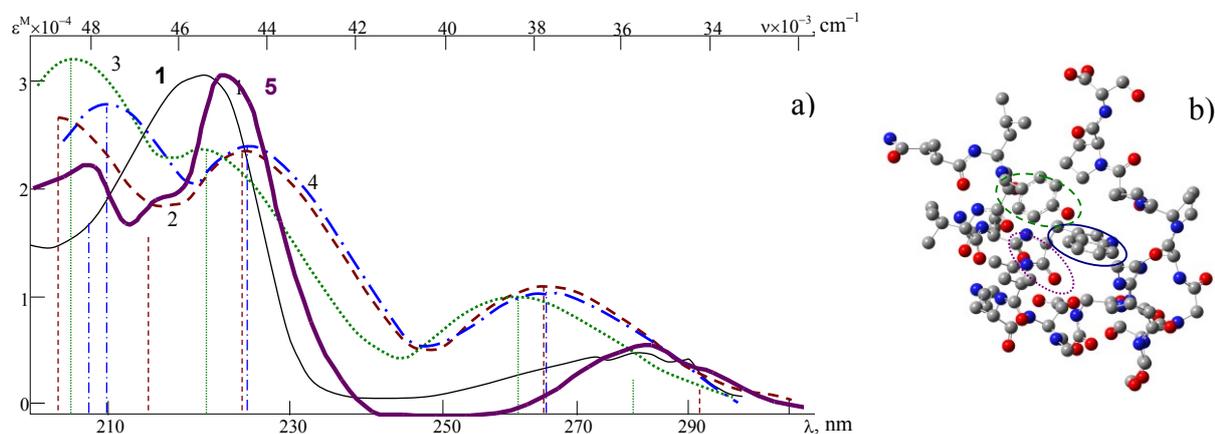
Fig.1. a) absorption spectrum of **tryptophan (1, thin solid curve) in the phosphate buffer, pH= 6,8 at 20°C**, model-spectra: single molecule (2, dashed), captured into cage (3, doted), and attached to polyethylene (4, dot-dashed), and **statistical spectrum of oscillating indole (5, thick graph)** of the unmovable trpcage. The sticks mark ε_{max}. b) trpcage spatial structure.

The tryptophan cage mini-protein (Fig. 1b) contains indole and phenol rings which are responsible for long-wave absorption and emission spectra. Spectral contour (Fig. 1a) and properties of this compound were obtained by applying the MD-CIS-elongation technique where whole system is calculated once but each oscillating indole conformer is recalculated.

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