Interaction and Localization of One-electron Orbitals in an Organic Molecule: Fictitious Parameter Analysis for Multi-physics Simulations

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We present a new methodology to analyze complicated multi-physics simulations by introducing a fictitious parameter. Using the method, we study quantum mechanical aspects of an organic molecule in water. The simulation is variationally constructed from the ab initio molecular orbital method and the classical statistical mechanics with the fictitious parameter representing the coupling strength between solute and solvent. We obtain a number of one-electron orbital energies of the solute molecule derived from the Hartree-Fock approximation, and eigenvalue-statistical analysis developed in the study of nonintegrable systems is applied to them. Based on the results, we analyze localization properties of the electronic wavefunctions under the influence of the solvent.

KEYWORDS: eigenvalue statistics, avoided crossings, quantum chaos, multi-physics simulation, variational construction of coupled simulation, electronic states of bio-molecules, one-electron orbital energy, solute-solvent system, RISM/SCF

The multi-physics simulation is one of the powerful methods to construct complex simulations representing realistic systems. Such a calculation is often constructed by combining multiple theories with different scales of description based on different approximations, e.g., climate simulations by fluid dynamics of the atmosphere surrounded by various external heat and humidity sources, quantum materials bound to classical large degrees of freedom, etc. Since reality and accuracy are required, those simulations have been larger and more complicated year by year. Then, guaranteeing their convergence and reliability becomes a more difficult problem.

In this letter, we study electronic states of a peptide in water obtained by a multi-physics simulation which consists of ab initio molecular orbital (MO) methods and classical statistical mechanics. The quantum chemical nature of large molecules in a solvent is also one of the most popular topics in physics and chemistry. In the present calculation, the simulation is constructed from a combination of the self-consistent field (SCF) calculation under the Hartree-Fock (HF) approximation and the statistical mechanics calculation by three dimensional version of the reference interaction site model (3D-RISM). Although the coupled simulation of RISM and SCF itself was developed in 1990’s and has been applied to several molecular systems, it attracts public attention again due to the recent developments of the distributed computing environments. Since the 3D-RISM/SCF coupled simulation heterogeneously couples the different theories both of which require large computational resources, the execution of the simulation for large solute molecules is difficult not only in an arrangement of the computer resources but also in theoretical aspects of computation such as stability of the convergence and reliability of the simulation.

The aim of this letter is two fold; one is to establish the methodology to ensure a proper execution of the complicated simulation, and the other is to introduce the new analysis for a electronic state of molecules using eigenvalue statistics. The target of our analysis is one-electron orbital energies $\varepsilon_j$ and its wavefunction $|\phi_j\rangle$ obtained as spatially independent wavefunctions under HF approximation. Although $\varepsilon_j$ and $|\phi_j\rangle$ are introduced through the variational minimization of the total energy, they still retain physical reality without Koopman’s theorem if we consider energies and wavefunctions of quasiparticles and quasiholes. Our key to accomplish these aims is an introduction of a fictitious parameter which can be used not only to investigate the stability and continuity of the results but also to perform sophisticated analyses based on the eigenvalue statistics.

At first, we construct 3D-RISM/SCF coupled simulation according to the standard variational way used in 1D-RISM/MCSCF. In the present calculation, the electronic states of the peptide are obtained by SCF under the restricted HF approximation (RHF), i.e., all electrons are assumed to configure closed orbitals. The variational functional is chosen as a total Helmholtz free energy $A(\lambda) = E_{\text{solute}}(\{|\phi_j\rangle\}) + \Delta \mu(\{|\phi_j\rangle\}; \lambda)$, (1) where $E_{\text{solute}}$ is an energy of the solute molecule and $\Delta \mu$ is the excess chemical potential of the solute obtained in 3D-RISM with the coupling strength $\lambda$. Statistical correlation functions of the solvent are calculated under the charge distribution of the solute represented by a set of the orbitals $\{|\phi_j\rangle\}$. The variation of the first term in r.h.s of (1) with respect to $|\phi_j\rangle$ gives usual SCF equations for the MO theory while the solvation effect is introduced through the second term. Variation with constraints using Lagrange multipliers gives conditions to be satisfied. Thus, the total free energy (1) of the coupled system is stabilized by solving these conditions.

One of the merits of the variational construction of complicated simulations is that a set of equations to be

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solved is given by a simple calculus once we define a functional of the whole system. In the present case, we only have to define the solute-solvent interaction potential

\[ u_\gamma(r; \lambda) = \lambda \sum_a \left[ q_a q_\gamma \frac{r_a}{r_{a\gamma}} + 4 \epsilon_{a\gamma} \left( \left( \frac{\sigma_{a\gamma}}{r_a} \right)^{12} - \left( \frac{\sigma_{a\gamma}}{r_a} \right)^{6} \right) \right] \]

(2)

where \( q_a \) is a point charge on a solute atom, \( q_\gamma \) is a partial charge on a solvent site \( \gamma \), \( r_{a\gamma} = |R_a - r| \) is a distance between the solute atom \( a \) and the solvent site \( \gamma \), \( \epsilon_{a\gamma} \) and \( \sigma_{a\gamma} \) is given by the standard parameter sets of Lennard-Jones potentials. We adopt the method of Mulliken population among several schemes to define \( q_a \),

\[ q_a = Z_a - \sum_{j=1}^{n/2} \sum_{\nu \in \gamma} \sum_{\nu'} \left[ C_{\nu j} C_{\nu' j} \langle \chi_\nu | \chi_{\nu'} \rangle + c.c. \right] \]

(3)

where \( C_{\nu j} \) are coefficients in a basis-set expansion of \( \left| \phi_j \right\rangle \)

\[ |\phi_j\rangle = \sum_\nu |\chi_\nu\rangle C_{\nu j} \]

(4)

by the atomic basis function \( |\chi_\nu\rangle \). This representation reduces computational costs of the whole simulation, and can be used even in large-scale simulations for proteins. Although the reduction of the cost is often a result of compensation in accuracy, it can be retained by combining other schemes of the potential representation.\(^{18}\)

After the variation with respect to \( C_{\nu j} \), the solvated Fock matrix element \( F_{\mu \nu} \) between \( \mu \) and \( \nu \) is given by

\[ F_{\mu \nu}(\lambda) = F_{\mu \nu}^{(0)} - \lambda V_{\mu \nu} S_{\mu \nu}, \]

(5)

where the overlap integral \( S_{\mu \nu} \) is defined by \( \langle \chi_\mu | \chi_\nu \rangle \). \( V_{\mu \nu} \) represents the environmental potential term induced by the partial charge distribution of water molecules,

\[ V_{\mu \nu} = \frac{1}{2} \int \left( \frac{1}{|R_\mu - r|} - \frac{1}{|R_\nu - r|} \right) Q(r; \lambda) \, dr, \]

(6)

where \( R_\mu \) and \( R_\nu \) represent atomic centers of the basis functions \( |\chi_\mu\rangle \) and \( |\chi_\nu\rangle \), respectively, and

\[ Q(r; \lambda) \equiv \sum_\gamma \rho_\gamma q_\gamma q_\gamma(r; \lambda) \]

(7)

is the partial charge distribution calculated by summing partial charges given by the distribution function \( q_\gamma(r; \lambda) \) over all the solvent sites \( \gamma \). We can numerically solve the Roothaan equation\(^4\)

\[ \mathbf{F}(\lambda) \mathbf{C} = \mathbf{S} \mathbf{C} \varepsilon \]

(8)

to obtain coefficients \( C_{\mu \nu} \) of the basis-set expansion as elements of the matrix \( \mathbf{C} \) and the orbital energies \( \varepsilon_j \) as diagonal elements of \( \varepsilon \).

The actual procedure to execute the coupled simulation is the following. The SCF calculation is performed from an appropriate initial distribution of the solvent. For the given distribution of partial charges of the solvent, the electron density is obtained after a convergence of the SCF. Then, 3D-RISM calculation to obtain \( g_s(r) \) is carried out using the charge distribution of the solute molecule. Converged \( g_s(r) \) determines the environmental term \( \lambda V_{\mu \nu} \) in the solvated-Fock matrix by which the SCF calculation is performed again. This procedure repeats until the whole distribution is converged. From the converged simulation, we obtain the solute electronic states and the solvent distribution functions.

Before entering the analysis using \( \lambda \), we show results of a methionine-enkephalin in two specific cases. This peptide consists of a sequence of 5 residues, Tyrosine, Glycine, Glycine, Phenylyalanine, and Methionine, with 75 atoms in total. From the standard SCF calculation, which corresponds to \( \lambda = 0 \), the orbital energies of the methionine-enkephalin are obtained in vacuum, while the fully-solvated case \( \lambda = 1 \) gives the orbital energies in aqueous solution. For the electronic ground state, we assume that 304 electrons occupy 152 independent spatial orbitals under RHF. Among several band-like structures in the orbital energies, we concentrate the analysis of the band just below the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), which contains 108 orbitals from 45th to 152th ones. Orbitals strongly localized on 1s atomic orbital of C, N, O, and 1s, 2s, 2p orbitals of S (known as core orbitals) can be found in the region far from the band we analyze. Since they exhibit almost no interaction with other orbitals, we do not consider these orbitals in the present analyses. The integrated density of states, \( D(E) = \sum \Theta(E - E_j) \), is shown for the band around HOMO and LUMO in Fig. 1. In this case, the 152nd orbital is HOMO and the 153rd is LUMO.

Despite that these orbital energies calculated from the generalized eigen-equation \( (8) \) are not usual eigenvalues defined in an autonomous system, they have almost the same property as the usual eigenvalues and eigenstates, i.e., the orbital energies are real, and the orbital states are orthogonal to the state with a different orbital energy. Moreover, repulsive interactions between them have the same origin as those of the eigenvalues.\(^{10}\) Thus, we can perform the eigenvalue-statistical analysis of these values after a certain unfolding procedure. In Figs. 2 (a) and (b), we show the integrated nearest-neighbor spacing distribution obtained after the standard procedure of unfolding the spectrum.\(^9\) It is known that the fully chaotic system shows the Wigner distribution while the regular system shows the Poisson distribution. For an intermediate case, we can compare the distribution to a Brody
Brody parameters obtained are obtained by normalization condition. The values of the wavefunctions to the fictitious parameter $\lambda$ slightly vary the parameter $\lambda$, i.e., avoided crossings $\lambda$ is not orthogonal between the orbital energies. Instead, we concentrate on the interaction between the orbitals when we slightly vary the parameter $\lambda$, i.e., avoided crossings between the orbital energies.

The Fock matrix (5) depends on the fictitious parameter $\lambda$ nonlinearly since $\lambda$ is also included in $V'_{\mu\nu}$, which is different from linearly perturbed systems. Even then, we can plot the orbital energies to the parameter as usual if we perform SCF calculations from $\lambda = 0$ (vacuum) to $\lambda = 1$ (fully solvated). Figure 3 is a plot of the orbital energies with respect to the parameter $\lambda$, where we chose $\lambda^2$ instead of $\lambda$ as the abscissa because of the nonlinear dependence on $\lambda$. Various sizes of avoided crossings are found in the figure, and there seems to be a small number of special orbitals which have almost no interaction with others. Such a separation of orbital states into groups without interaction each other can lead to smaller values of the Brody parameter.

The separation of eigenfunctions is often seen in the intermediate semiclassical limit of quantum chaotic systems, i.e., statistical properties in a range around a finite energy. A stadium billiard system has a series of eigenfunctions corresponding to a bouncing-ball orbit by which the nearest-neighbor spacing deviates from the ideal case of random matrix systems. The eigenstates corresponding to the bouncing-ball orbit is extremely localized in momentum space. In the present results, such localization can be observed in the coordinate space. Actually, the core orbitals, which we have removed from the Brody analysis, are strongly localized on a certain atomic basis function. Although the orbitals in the region we study here do not localize so strong, it is reasonable to analyze the property of orbital states with respect to the localization on the atomic basis functions.

In order to analyze the extent of localization, we define the degree of delocalization of $j$-th orbital state by

$$W_j = \frac{\left| \sum_{\nu} |C_{\nu j}|^2 \right|^2}{\sum_{\nu} |C_{\nu j}|^2}$$

through the basis-set expansion coefficient $C_{\nu j}$ in (4). This is a representation-dependent quantity, and we define $W_j$ on the standard atom-centered basis set $\{ |\chi_{\nu}\rangle \}$ in the present work. Although $\{ |\chi_{\nu}\rangle \}$ is not orthogonal

Fig. 2. The integrated distribution of the nearest-neighbor spacing of the orbital energies of a met-enkephalin (a) in vacuum and (b) in water. We also show histograms for the nearest-neighbor spacing in the insets, where curves show the Brody distribution (see text) with (a) $q = 0.52$ and (b) $q = 0.33$.

Fig. 3. One-electron orbital energies near the highest occupied molecular orbital. The abscissa is $\lambda^2$, the square of the coupling strength between the solute and solvent.
each other and we cannot relate the coefficients $C_{ij}$ directly to the extent of the spatial distribution, the value of (11), the approximate number of basis functions contained, still represents the relative strength of the delocalization. In Fig. 4, we show the distribution of (11). It can be seen that the distribution has two peaks over the whole values of $\lambda$ while the places of the peaks slightly change. That is, the orbitals are divided into two groups: relatively localized orbitals ($0 < W_j < 60$) and delocalized orbitals ($60 < W_j < 130$). This separation of orbitals is considered to be the reason why the Brody parameter exhibits the intermediate values.

Before summarizing this work, we give some comments for future studies. Since our analysis is based on the parameter variation, more sophisticated analysis such as the level-curvature analysis and distribution of gap sizes of avoided crossings\textsuperscript{15,16} can be performed. Since these properties are known to be sensitive for intermediate dynamical systems, it will be more appropriate for analyzing molecular systems. By the use of these analysis, it is desirable to investigate quantum aspects of large molecules in water. When we investigate large systems such as proteins or nucleic acids, more effective methods must be needed. One of such methods is the fragment MO calculation\textsuperscript{24} by which the orbital energies can be obtained with small errors.\textsuperscript{25}

Another interesting problem is whether the regularity of the quantum many-body system is influenced by solvation effects or not, while in the present work we have concentrated on the localization of molecular orbitals. Although we could not give a clear answer within our Brody analysis, such analysis on the regularity will be performed through the detailed analysis of nodal patterns, Husimi representation, etc. of the orbital wavefunctions with respect to the fictitious parameter. Introducing the parameter enables us to assign each solvated orbital in terms of the orbitals in vacuum. This procedure will successfully be done by connecting characteristic features of the orbital over avoided crossings since it is possible even in strongly chaotic systems\textsuperscript{13} if many pairwise avoided crossings are found. From a technical point of view, the continuous parameter is also important as a computational technique. In our case, the stability of the result is numerically supported by varying the parameter slightly, since physically meaningful quantities can only be obtained as stable results under small perturbations. In order to obtain stable and significant results from complicated realistic simulations, the fictitious parameter approach will be one of the powerful methods.

In summary, we have studied statistics of the orbital energies and localization of orbital states through the variation of the fictitious parameter. This is our first report on the eigenvalue-statistical analysis of the orbitals as a new approach to quantum many-body systems. We hope that these new methods will be used to study quantum aspects of large bio-molecules as well as to complete large-scale realistic simulations.

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