Abstracts of Invited and Contributed Talks, Sep. 8

8A1-1I

Theoretical Studies on Photoinduced Charge Separation of Molecular Hetero-Junction and Dye-Sensitized Solar Cells

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I will discuss our theoretical studies on the optical and electronic process that take place in organic solar cells. First, in order to obtain the design rules of conjugated polymer required for improved molecular electronics, the charge transport properties at different organic-organic semiconductor interfaces (TFB/F8BT) are studied based on *ab initio* quantum master equations. The results suggest a mechanism of exciton-migration followed by a hole back transfer addition to a simple charge-transfer, which leads to a red-shifted and longer-lived emission of F8BT. Secondary, I will discuss about several new transitions due to the interfacial charge transfer found for the TCNE/TiO_2 dye-sensitized solar cells. The surface complex of TiO_2 nanoparticles and TCNQ are studied based on DFT calculations and the structure of the surface complex optimized shows an IR spectrum analogous to the experimental spectrum. From TDDFT calculations based on this optimized structure, we show that the interfacial charge transfer transitions from the HOMO of the surface-bound TCNQ molecules to the unoccupied levels of the TiO_2 nanoclusters occur in the visible to near IR region. Finally, recombination in dye-sensitized solar cells with direct injection which is cast as internal conversion will be discussed. For catechol-thiophene dyes with 1, 2, or 3 thiophene units, the complex reproduces the previously observed dye-to-semiconductor bands. Based on *ab initio* calculations, we compare the decomposition of the internal conversion rate by vibrational mode and predict a trend in recombination with the extension of conjugation, which offers an explanation for the trend in DSSC efficiency. We also analyze derivative coupling constants in dyes NK1 (2E,4E-2-cyano-5-(4-dimethylaminophenyl) penta-2,4-dienoic acid) and NK7 (2E,4E-2-cyano-5-(4-diphenylaminophelyl) penta-2,4-dienoic acid) and relate them to the different dynamics that was observed for these dyes on TiO_2.

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8A1-3I

Orbital theories for molecular electronic devices

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Ballistic electron transport through molecules occurs, for instance, in molecular electronic devices (MEDs). In MEDs, two external contacts are connected to a molecule and the current is measured as a function of the applied voltage. Ballistic transport is characterized by the absence of coupling between electronic and nuclear degrees of freedom so that the coherence of the electronic wave function is preserved across the molecule. Theories of MEDs are quite involved in general, requiring advanced Green's function techniques. However, various prominent features of MEDs can be understood drawing only on elementary quantum theory. To support this point of view, we discuss simple models [1-4] which enable one to reproduce and predict key features of MEDs. We present, for example, a two component orbital theory. In this theory, the device orbitals (DOs) are written as a two component wave function, each of which is much simpler to construct than the combined orbital. Using these DOs, the conductance can be calculated drawing on the source-sink potential approach [1]. To illustrate our theory, we apply it to explain the conductance suppression in cross-conjugated systems and the dependence of the conductance on the contact position in aromatic systems. Furthermore, we apply our models to analyze the conductance of finite graphene flakes of varying shapes and sizes. We establishing simple concepts relating the structure of the graphene flakes to their conductance.

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8A1-5I

Molecular electronics and ultrafast DNA sequencing

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Delicate modulation of the molecular orbitals in molecular systems is useful to tune the performance of electron/spin transport. Not only electric and magnetic fields are powerful means for that purpose but also the characteristic change in conductance due to intermolecular interactions such as pi-pi stacking can be utilized for molecular sensing. Thus, we discuss the effects of external fields on molecular electronic and spintronic devices. Electron/spin transport phenomena in molecular electronic/spintronic devices [1] and graphene nanoribbon spin valves [2] are discussed based on density functional theory (DFT) coupled to non-equilibrium Green function theory (NEGF). The non-collinear spin states for the open systems are fully taken into account in a self-consistent manner with the non-equilibrium Green's function approach by using the Postrans program package [1-3]. A graphene nanoribbon (GNR) spin-valve device shows the super magnetoresistance behavior as a spin filter which selectively transmits almost 100% spin-polarized current [2]. Given that GNR electrodes show pristine molecular characteristics much better than Au or Ru electrodes [4], we find that measuring two-dimensional conductance spectra of a graphene [5] or GNR placed across a fluidic nanochannel leads to a powerful ultrafast DNA sequencing method [6]. In this device, while a single-stranded DNA (ssDNA) passes beneath the GNR, a single base interacts with the GNR via π-π stacking, giving a sharp conductance change. To explain the operation principle for sequencing the target ssDNA bases, we performed four step theoretical calculations. First, the binding energies between each DNA base and GNR are investigated from *ab initio* quantum chemical calculations. Second, the molecular dynamics study was performed in the realistic manner including the temperature effects, solvent molecules, and counter ions. Third, the electron transport properties of DNA base-GNR complex are studied by the DFT-NEGF method to understand the origin of conductance differences between DNA bases. Finally, we clarified the sequence of the target ssDNA via our data-mining technique and two-dimensional transient autocorrelation functions. This reliable ultrafast sequencing method would revolutionize the future bioinformatics and genetics.

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8A2-1I

Oxidative dehydrogenation of a terminal water at the rutile TiO_2(110)-water interface

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Oxidative dehydrogenation (ODH) of a H_2O molecule is enormously costly, taking 2.7 eV. Deprotonation requires 0.8 eV. The difference is still large enough to give the hydroxyl radical a daunting oxidative power of 1.9 V *vs* SHE. Will adsorption on a transition metal oxide surface bring the ODH energy down? If so, will this not also decrease the reduction potential of the adsorbed OH radical product? We have investigated this question using a combination of density functional theory based molecular dynamics (DFTMD) and free energy perturbation methods. The model metal oxide system is the much studied rutile TiO_2(110)-water interface. Using PBE, the surface ODH energy was indeed found to be lower than in solution. Resolving in a deprotonation and oxidation free energy, revealed that the increase in acidity of a terminal H_2O relative to solution[1] is an important factor in the H_2O activation. The oxidation potential of the OH radical was found, somewhat surprisingly, to be almost the same. The surface ODH energy is not directly available from experiment. We can however use the solution data mentioned above as validation. Unfortunately our reduction potential of the aqueous OH radical is too small by as much as 0.6 V[2]. This effect is now generally understood to be the result of the tendency of the generalized gradient approximation (GGA) to delocalize holes in O2p orbitals. For the same reason the GGA pushes the valence band maximum in TiO_2 up by 0.8 eV[3]. For the surface ODH reaction the delocalization error even leads to the formation of the wrong species, namely an adsorbed hydroxide anion plus delocalized hole in the valence band, rather than an hydroxyl radical. These observations cast serious doubt on the PBE results. Only recently we were able to make progress thanks to the development of efficient methods for the implementation of exact exchange under periodic boundary conditions[4]. DFTMD simulation using the HSE screened hybrid functional, indeed traps the hole with localization energies of 0.5 eV or more. This talk will be a brief review of our DFTMD methodology together with the presentation of some of the latest results obtained with HSE.

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8A2-3C

Adsorption and excitation of black-dye on TiO_2 anatase (101) surface for dye-sensitized solar cells

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Dye-sensitized solar cells (DSSC) are expected as a cost effective next generation solar-to-electricity energy conversion devices [1]. The efficiency of the power conversion is greater than 10% when Ru(II) polypyridyl dyes are used and increasing the efficiency of the DSSC is very important issue as academic and industrial interests. To understand a photoexcited electron transfer process, an initial step of the energy conversion of the DSSC, we investigate possible adsorbed structures of black-dye on TiO_2 anatase (101) surface and excited states of the black-dye molecules.

To obtain the adsorbed structures, geometry optimizations were carried out using DFT method (BLYP functional) with plane wave basis. For excited state calculations of black-dye molecule, TDDFT method (B3LYP functional) was used with Gaussian basis.

We considered four possible adsorbed structures, two of them are bound to surface by one carboxyl group (one-leg) and the other two are bound with two carboxyl groups (two-legs). Regarding the adsorbed structures of Ru(II) polypyridyl dyes such as N3 dye, three-legs structure with one of a proton of carboxyl groups transferred to surface has been regarded as a most stable structure rather than one-leg and two-legs structures. In this study, we found that the one-leg structure with the proton retained on a carboxyl group of the black-dye was more stable than two-legs structures (Fig. 1). This is attributed to the presence of the hydrogen bond between hydrogen atom of carboxyl group and oxygen atom of surface.

We also investigated the excited states of isolated and adsorbed structures of the black-dye molecules and compared with the UV-visible spectra. In adsorbed structures with a proton retained on the dye, the planar structure of the terpyridine ligand was distorted from the isolated one, causing red shift of the UV-visible spectra. We examined Kohn-Sham orbitals related to the large peaks and found that the main configurations of the excited states were delocalized orbitals on terpyridine ligand. These delocalized characters are responsible for the good performance of the Ru(II) polypyridyl dyes.

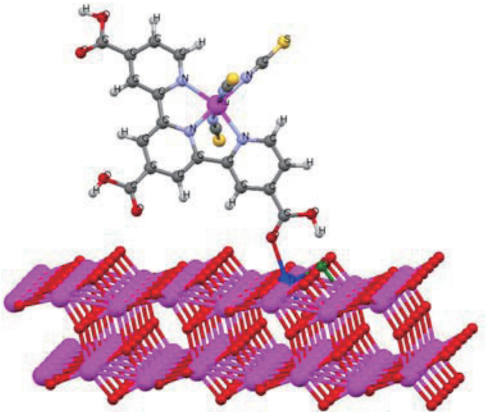

Figure 1. Adsorbed structure of black-dye on TiO_2 anatase (101) surface of one-leg protonated form.

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8B1-1I

Real-time TDDFT calculation in molecules and solids

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We have been developing a computational method to solve the time-dependent Kohn-Sham equation in real time and real space to describe electron dynamics induced by optical field. The method may be applied to both isolated molecules and bulk periodic solids. In the presentation, I would like to present our recent progresses with the method taking examples from both molecules and solids.

In molecules, we have recently developed a real-time computational method for magnetic circular dichroism (MCD) [1]. In our framework, we solve the time-dependent Kohn-Sham equation under a finite magnetic field. We may thus obtain the MCD spectra of both discrete and continuum region without any perturbative expansion.

In periodic solids, we may describe nonlinear electron dynamics in dielectrics induced by an ultrashort laser pulse. We show our recent application to explore a generation mechanism of coherent phonon in typical dielectrics, Silicon [2]. It has been invoked that there are two mechanisms in coherent phonon generation, the impulsively stimulated Raman scattering induced by a virtual electronic excitation during the irradiation of the laser pulse, and the displacive excitation through a real excitation of electrons. We show that the time-dependent density functional theory describes both mechanisms in a unified way.

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8B1-3I

Photoinduced Electron Dynamics in Nanostructures: Nonuniform and Self-Consistent Light-Matter Interactions

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In the conventional optical responses of molecules, wavelengths of the lights are usually considered to be much longer than molecular sizes. Thus, a target molecule is well approximated by a point dipole and the dipole feels an almost uniform electromagnetic field. This condition underlies the conventional dipole approximation. Furthermore, light is an external field to excite molecules and its wavelength is definitely determined by an apparatus condition. Since spatial resolution of spectroscopy is limited by the wavelength of the incident light, it is impossible to gain molecular properties in a local region shorter than the wavelength, i.e., diffraction limit. However, recent development of nanofabrication and nano-optical techniques requires a more general optical response theory fully taking account of nonuniform and self-consistent light-matter interactions.

First, a generalized theoretical description of a light-matter interaction beyond a dipole approximation is developed on the basis of the multipolar Hamiltonian with the aim of understanding the near-field excitation in nanostructures[1]. The theory is formulated for a system consisting of a molecule and a near-field, where a nonuniform electric field plays a crucial role. A nonuniform electronic excitation of a molecule is demonstrated by solving a time-dependent Kohn-Sham equation in real-space and real-time [2,3] with an implementation of the nonuniform light-matter interaction.

Second, optical forces induced by a near-field are calculated for a 1 nm-sized metal particle mimicked by a jellium model fully taking account of multipole interaction [4]. A highly localized near-field nonuniformly polarizes the metal particle. The locally induced polarization charges in the molecules are partly canceled by the screening charges. The polarization and screening charges generally contribute to the attractive and repulsive forces, respectively, and a sensible balance between these charges results in several peaks in the optical force as a function of the frequency of the near-field. The resonance excitation does not necessarily maximally induce the net force and the force exerted on the molecules strongly depends on the details of their electronic structures.

Finally, I will discuss our recent research activity of electron and electromagnetic field coupled dynamics in nanostructures.

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8B1-5I

An efficient non-pairwise-additive correlation energy functional for dispersion forces

John F. Dobson and Tim Gould

We use the continuum mechanics (CM) of Tao, Gao, Tokatly and Vignale [PRL **81**, 195106 (2010)] to describe electronic response of inhomogeneous electronc systems to effective fields. We thereby obtain an approximation to the RPA correlation energy that is computationally efficient and describes long-ranged (e.g. van der Waals) correlations beyond the pairwise-additive approximation. So far this approach has been tested successfully on the case of two thin parallel metal slabs at all separations D down to overlap of the electronic clouds [ArXiv:1106.0327v2]. Our method reproduced full (d)RPA results well for all D values, and gave the correct asymptote $E = -CD^{-5/2}$ at large separations $D \rightarrow \infty$, in contrast to the present generation of efficient van der Waals functionals. The CM theory also gives the exact response of quantal one-electron systems. Development of the method for periodic systems is underway.

8B2-1I

Analytic calculations of anharmonic effects in vibrational spectra

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Anharmonic effects are small, but can make important contributions to a wide range of vibrational spectroscopies. With the advent of nonlinear vibrational spectroscopies, these anharmonic effects can be directly probed [1,2].

Computationally, the calculation of anharmonic corrections to vibrational spectra and nonlinear vibrational spectroscopies is complicated due to the need for calculating higher-order energy derivatives with respect to geometrical perturbations. Calculations of anharmonic effects are almost exclusively done in a mixed analytical-numerical scheme [3,4], although an analytic implementation including up to quartic force constants was presented at the Hartree–Fock level of theory by Handy and coworkers twenty years ago [5].

In this talk, I will present our recent efforts in obtaining an analytic approach for calculating the necessary energy derivatives analytically, both at relativistic and non-relativistic levels of theory [6]. In addition to a brief presentation of the theoretical framework, I will present sample calculations of anharmonic effects in various linear and nonlinear vibrational spectroscopies.

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8B2-3C

Anharmonic vibrational theory for large polyatomic molecules

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I. Introduction

A combination of the electronic structure and vibrational theories has made feasible a computation of molecular vibrational structure from the first principles. The computation of vibrational energy levels is extremely important not only for aiding in experimentalists to interpret vibrational spectra, but also for understanding the thermodynamics and chemical reactions. We have developed an efficient generator of the molecular potential energy surface (PES) and a solver of the vibrational Schrödinger equation. The developed method is applied to biological molecules with more than 100 degrees of freedom. The usefulness of theory is discussed with a focus on a complex vibrational spectrum of hydrogen bonded systems.

II. Methods

The PES is generated on-the-fly using an electronic structure program in a fully automated way. The method initially generates a quartic force field (QFF) by a finite differentiation of Hessian matrices using a low-level, electronic structure method. Then, the QFF coefficients are employed to evaluate the strength of mode coupling terms [1], and those that are found to be important are improved by replacing the QFF by a more accurate function based on a high-level, electronic structure theory. This scheme exploits a multiresolution technique [2] for combining different types of functions and electronic structure methods in a single PES. The implementation makes use of a massively parallel architecture, in which the electronic structure calculations for each grid point are distributed among different nodes.

Vibrational quasi-degenerate perturbation theory (VQDPT) [3] is developed based on a vibrational self-consistent field reference for the ground state (zero point). The method incorporates a strong vibrational resonance by the configuration interaction (CI) and the remaining weak interactions by the perturbation theory. VQDPT is faster than a conventional CI more than 100 times without a loss of accuracy.

III. Applications

The developed methods mentioned above are applied to a series of biologically relevant molecules: nucleic acid bases and base pairs, guanosine, their cluster with waters, and polypeptides.

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8C1-1I

Towards quantum chemistry on quantum computers

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Quantum computers have a potential to change the way quantum chemistry is done. For example, they are able to efficiently find the exact solution of many-body Hamiltonian eigenvalue problem [1]. As was shown in the seminal work by Aspuru-Guzik et. al. [2], quantum computers, if available, would be able to perform the full configuration interaction (FCI) energy calculations with only a polynomial scaling, in contrast to conventional computers where FCI scales exponentially. Of course, experimental realization of large enough quantum computers is an extremely difficult task. However, first step towards this goal, calculation of H_2 in a minimal basis on a real quantum computer, has been reported recently by Lanyon et al. [3]

This lecture will summarize our work in the field of interconnection of quantum chemistry and quantum computing [4]. Improved version of the quantum full configuration interaction (QFCI) method, which uses the iterative phase estimation algorithm and its application to non-relativistic as well as relativistic configuration interaction (CI) energy calculations will be presented.

As far as non-relativistic CI calculations are concerned, simulations (on a conventional computer) of QFCI calculations of the four lowest lying electronic states of methylene molecule (CH_2), which exhibit a multireference character were performed [4]. It has been shown that with a suitably chosen initial state of the quantum register, one is able to achieve the probability amplification regime of the iterative phase estimation even for nearly dissociated molecule. Concerning the relativistic calculations, we have performed simulations of the quantum computing analogue of the Kramers-restricted CI calculations for the SbH molecule. A minimalistic example of a quantum circuit performing such a calculation, which might become experimentally realizable in the near future, will be presented. Last but not least, possible use of genetic algorithms in the design of quantum circuits for QFCI calculations will be discussed.

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8C1-3I

Advances in Multireference Coupled Cluster Theory

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A state-specific and rigorously size-extensive multireference coupled cluster theory (Mk-MRCC) and a companion second-order perturbation theory (Mk-MRPT2) have been developed into powerful and practical tools for chemical research. The effectiveness of our Mk-MRCC methods is established by extensive computations on benchmark systems, including the low-lying electronic states of O_2, CH_2, HCF, and H_2CO, the dissociation of F_2, and the problematic ozone molecule. In chemical applications of Mk-MRCC theory, outstanding results have been obtained for the optimum geometric structures, vibrational frequencies, and electronic excitation energies of the organic diradicals *ortho*-, *meta*-, and *para*-benzyne, as well as the cyclic polyenes cyclobutadiene and cyclooctatetraene. A rigorous Mk-MRCC torsional surface has been generated for the classic problem of the stereomutation of cyclopropane. The seemingly simple organic molecule cyclobutanetetraone (C_4O_4) is demonstrated by Mk-MRCC theory to actually have a triplet rather than a closed-shell singlet ground state! Finally, joint theoretical and experimental work is presented on novel hydroxycarbenes (RCOH; R = H, CH_3, and phenyl) that has led to the first isolation and identification of these species. These hydroxycarbenes show rapid tunneling ($t_{1/2} \approx 2$ hrs) at 11 K through prodigious energy barriers of almost 30 kcal mol^{-1}, a remarkable phenomenon confirmed by our high-accuracy computations of barrier penetration integrals.

8C1-5I

Advanced multireference quantum chemistry with large active space

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We will present our recent progress in the development of efficient multireference approaches based on the density matrix renormalization group (DMRG) method and its partner dynamical correlation models. Following Chan's successful adaptation of the DMRG algorithm to *ab initio* quantum chemistry calculations, we use it to describe a substantial amount of static correlation accurately with large active space for multireference calculations, e.g. CAS(28e,32o) or even larger. Developing our efficient implementation of the DMRG method, we recently demonstrated its significant applicability to challenging multireference chemistry, involving strongly-correlated electronic states of transition metal complexes and π-conjugated molecules. For the latter, we will show some novel findings in spin structures of polycarbenes (orgnaic magntic molecules) and graphene-nanoribbons (future organic semiconductors). These electronic structures associated with complex multireference electron correlation are thought to be a key to understand interesting quantum phenomena arising in organic materials and biomolecules.

Dynamic correlation needs be taken into account to deliver a quantitative accuracy in calculations, and is regarded as weak correlation that should be handled perturbatively in light of efficiency. We have developed a joint theory of the DMRG method and a canonical transformation (CT) idea to calculate the dynamic correlation on top of multireference description with large active space. Our CT theory constructs a renormalization structure of the high-level dynamic electron correlation in an effective Hamiltonian where the bare Hamiltonian is transformed by the unitary exponential correlation operator. As an alternative efficient routine to approach the dynamical correlation problems, we have recently developed a novel extension of DMRG which has led to its combination with the CASPT2 method. We will discuss some theoretical aspects of the DMRG-CT and DMRG-CASPT2 theory and their applications to quasi-degenerate electronic states in chemistry.

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8C2-1C

Study of Simulation Method of Time Evolution in Rigged QED

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We discuss how we can formulate time evolution of physical quantities in the framework of the Rigged QED (Quantum ElectroDynamics) [1]. The Rigged QED is a theory which has been proposed to treat dynamics of charged particles and photons in molecular systems in a quantum field theoretic way. In addition to the ordinary QED which is Lorentz invariant with Dirac (electron) field and U(1) gauge (photon) field, Schrödinger fields which represent nuclei are added. In this way, dynamics of nuclei and their interaction with photons can be treated in a unified manner. To solve the dynamics in the Rigged QED, we need different techniques from those developed for the conventional QED. As a first step toward this issue, we propose a procedure to expand the Dirac field operator, which represents electrons, by solutions of the Dirac equation for electrons in nuclear potential [2] and derive time evolution equations for the creation and annihilation operators.

We expand Dirac field operator as $\hat{\psi}(ct,\vec{r}) = \sum_{n=1}^{N_D} \sum_{a=\pm} \hat{e}_{n^a}(t)\psi_{n^a}(\vec{r})$. Here, $\psi_{n^a}(\vec{r})$ is a normalized orbital obtained by solving the Dirac equation, n is a label for the orbital whose superscript a denotes electron (positron) orbital when $+(-)$. $\hat{e}_{n^+}$ is the electron annihilation operator and $\hat{e}_{n^-}$ is the positron creation operator. The Dirac field equation can be expressed as $i\hbar\gamma^\mu \hat{D}_{e\mu}(x)\hat{\psi}(x) = m_e c\hat{\psi}(x)$ with the gauge covariant derivative $\hat{D}_{e\mu}(x) = \partial_\mu + i\frac{Z_e e}{\hbar c}\hat{A}_\mu(x), \quad Z_e = -1$ where $\hat{A}_\mu(x)$ is the gauge field operator. We derive time evolution equation for the annihilation/creation operator from this equation. (At this stage, we adopt the adiabatic approximation for the nuclear motion, namely neglecting "the Rigged current", for simplicity.)

We also discuss how time evolution of physical quantities can be calculated using this equation. In particular, we discuss "local refractive index", which may provide a new viewpoint for molecular chirality, can be defined by the time evolution of polarization and magnetization operators.

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8C2-2I

Analytical Principles and the Evolution of Physical Laws

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Abstract

In preceding accounts [1,2] we have advanced a retarded-advanced sub-dynamics transcending standard probabilistic formulations providing a wide-range of interpretations. The contradiction between time reversible microscopic physical laws and the irreversible nature of thermodynamical equations are examined from this standpoint. The subjective nature of statistical mechanics in connection with a theoretical formulation relative to a given level of description, is also re-examined. A complex symmetric ansatz, incorporating both time reversible and time irreversible evolutions discloses the evolution of the basic laws of nature and reveals new orders of organization. Examples are given from the self-organizational behaviour of complex biological systems as well as background dependent relativistic structures including Einstein's laws of relativity, the time delay, the gravitational redshift and the perihelion movement of Mercury. A promising solution to the present conundrum is provided by a specific informity rule in combination with a Gödelian like rule of decoherence code protection. The theory gives an interesting cosmological scenario in absolute agreement with the second law.

[1] E. Brändas, Mol. Phys. **108**, 215 (2010).
[2] E. Brändas, Int. J. Quant. Chem. **111**, 215 (2011).