Breakthrough Design and Implementation of Electronic and Vibrational Many-Body Theories

Final Scientific/Technical Report DE-FG02-04ER15621

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1. Final Scientific/Technical Report

1.1. Publications

Twenty-three (23) publications[1-23] and four (4) conference proceedings[24-27] have resulted from the PI's group during the last funding period (November 1, 2007 through October 31, 2010) of the Department of Energy (DOE) award. Four of them are invited articles or reviews,[4,8,18,19] four are invited book chapters,[9,21-23] two are cover articles (**Fig. 1**),[8,19] two are among *J. Chem. Phys.* monthly most downloaded articles and cited more than 20 times since 2008,[2,10] and one is the *J. Chem. Phys.* Editor's Choice.[15] The PI is a Guest Editor of the Special Issues[28,29] in honor of Kimihiko Hirao in *Int. J. Quantum Chem.* (2009) and of the 50th Anniversary Issue of *Theor. Chem. Acc.*

Fig. 1. Cover articles reporting work supported by DOE.

1.2. Presentations

During the same period, the PI was an invited speaker at nineteen (19) international and domestic conferences (including ISTCP, WATOC, TACC, CCTCC, ACS, and ICQC) and twelve (12) university and national laboratory seminars (including Georgia Southwestern State, Cornell, Mississippi, Southern California, Urbana-Champaign, Emory, Florida State, Washington State, Pacific Northwest, and Puerto Rico). The PI was a plenary speaker in one of the conferences (SERMACS) and an invited poster presenter in the Hewlett-Packard Outstanding Junior Faculty Awardees session in the 235th National ACS Meeting. Graduate students supported by DOE also made numerous presentations. The PI was also a co-organizer of the Sanibel Symposia (2008, 2009, and 2010) and a symposium in the 241st National ACS Meeting (2011).

1.3. The Principal Investigator Recognitions

The PI's work has been recognized by the following awards: the Hewlett-Packard Outstanding Junior Faculty Award (2008), the Medal of the International Academy of Quantum Molecular Sciences (2008), the National Science Foundation CAREER Award (2009), and the Camille Dreyfus Teacher-Scholar Award (2009). The Medal is the highest international award given to a quantum chemist or physicist age 40 or younger. The PI has also been appointed as members of the Editorial Advisory Boards of *Phys. Chem. Chem. Phys.* and *Theor. Chem. Acc.*

1.4. Students and Postdoctoral Researchers Recognitions

The members of the PI's group supported by DOE have been recognized by awards, degrees, and faculty appointments. Dr. Muneaki Kamiya (postdoctoral researcher) has been appointed as Assistant Professor in Gifu University, Japan. Toru Shiozaki (graduate student) has been awarded a Fellowship from the Japan Society for the Promotion of Science, a Research Award from the University of Tokyo, a Poster Award from the 3rd Asian-Pacific Conference on Theoretical and Computational Chemistry, a Best Presentation Prize from the Annual Meeting of Japan Society for Molecular Science, a WATOC 2008 Poster Prize, and an ACS Graduate Student Award in Computational Chemistry. Shiozaki has obtained M.Sc. (2008) and Ph.D. (2010) from the University of Tokyo. Murat Keçeli (graduate student) has won the Best Poster Prize from the 18th Conference on Current Trend in Computational Chemistry. Olaseni Sode (graduate student) has won the Best Poster Award from the 2009 Sanibel Symposium. Undergraduate member, Michael Durante, received a funding from the University Scholars Program.

1.5. Research Highlights I. Electrons

Grid-based Hartree–Fock equation solver.[1] Numerical solutions of the Hartree–Fock (HF) equation of polyatomic molecules have been obtained by an extension of the numerical grid-based density-functional method of Becke and Dickson.[30,31] The action of kinetic energy (Laplace) operator on numerical orbitals is evaluated by a finite-difference method. Poisson's equation for the Coulomb and exchange potentials is also solved numerically on the grid.[32] The grid places a large number of radial points near nuclei and can thus account for the cusps in the HF wave functions at nuclei. The method can achieve accuracy of 10^{-5} E_h in total energies of small molecules in the gas phase without extrapolation, which is higher than achievable with the aug-cc-pV5Z basis set by two orders of magnitude.

Explicitly correlated coupled-cluster and perturbation methods.[4,6,10,15,18] The algebraic expressions defining high-rank coupled-cluster (CC) methods that include interelectronic distances (r_{12}) explicitly (F12-CC)[18,33-36] have been derived with the aid of computerized symbolic algebra SMITH.[4] Efficient computational sequences to evaluate these expressions have also been suggested and computer implemented by SMITH.[6,10] These implementations—F12-CCSD, F12-CCSDT, and F12-CCSDTQ as well as explicitly correlated second-order perturbation method (F12-MP2)[37]—take into account point-group and index-permutation symmetries. In addition to automating tedious symbolic manipulation processes inevitable in CC derivation and implementations,[38-40] SMITH performs additional algebraic transformation steps specific to the F12 methods, i.e., the identification and isolation of high-rank molecular integrals involving the r_{12}-dependent factor and the resolution-of-the-identity insertion[41,42] to facilitate their evaluation.

Combinations of CC and perturbation methods constitute one of the most powerful classes of methods to describe dynamical and even nondynamical electron correlation.[43] Second- and third-order perturbation corrections to F12-CCSD and F12-CCSDT in the excitation manifold of triples and

Ne	
Grid-based HF (our work)	−128.54710
CCSDT-F12/aug-cc-pCV5Z (our work)	−0.39008
aug-cc-pV6Z correction (our work)	−0.00040
CCSDTQ-F12 correction (our work)	−0.00010
Correlation energy (our work)	−0.3906 ± 0.0004
Correlation energy (Chakravorty *et al.*)	−0.39047
Total energy (our work)	−128.9377 ± 0.0004
Total energy (Chakravorty *et al.*)	−128.9376
Total energy (Gdanitz)	−128.93701
BH	
Grid-based HF (our work)	−25.13164
CCSDT-F12/aug-cc-pCV5Z (our work)	−0.15743
CCSDTQ-F12 correction (our work)	−0.00009
Correlation energy (our work)	−0.1575 ± 0.0002
Total energy (our work)	−25.2892 ± 0.0002
Total energy (O'Neill and Gill)	−25.2879
FH	
Grid-based HF (our work)	−100.07080
CCSDT-F12/aug-cc-pCV5Z (our work)	−0.38793
CCSDTQ-F12 correction (our work)	−0.00022
Correlation energy (our work)	−0.388 ± 0.001
Correlation energy (O'Neill and Gill)	−0.389
Correlation energy (Harding *et al.*)	−0.3892
Total energy (our work)	−100.459 ± 0.001
Total energy (Lüchow and Anderson)	−100.458 ± 0.005
Total energy (Harding *et al.*)	−100.4601
H_2O	
Grid-based HF (our work)	−76.06559
CCSDT-F12/aug-cc-pCVQZ (our work)	−0.37074
CCSDTQ-F12 correction (our work)	−0.00036
Correlation energy (our work)	−0.371 ± 0.003
Correlation energy (O'Neill and Gill)	−0.371
Total energy (our work)	−76.437 ± 0.003
Total energy (Bytautas and Ruedenberg)	−76.4390 ± 0.0004
Total energy (Harding *et al.*)	−76.4388

Fig. 2. Nearly exact energy solutions of the Schrödinger equations (in E_h).

quadruples have been formulated and computer implemented with the aid of SMITH.[15] They form another rapidly converging sequence of electron-correlation methods: F12-CCSD, F12-CCSD(T), F12-CCSD(2)$_T$, F12-CCSD(3)$_T$, F12-CCSDT, F12-CCSD(2)$_{TQ}$, F12-CCSDT(2)$_Q$, and F12-CCSDTQ in the order of increasing accuracy and complexity, where the integers in the parentheses are the order of perturbation and T and Q stand for triple and quadruple excitation manifolds. We have also reported equations and computational sequences of explicitly correlated equation-of-motion coupled-cluster (F12-EOM-CC) methods up to quadruple excitations.[4]

The F12-CC methods developed by us form one of the most rapidly converging series of approximations toward the exact solutions of Schrödinger equations with respect to both the highest excitation rank and basis-set size. Using the Slater-type r_{12}-dependent factor, 1−exp(−
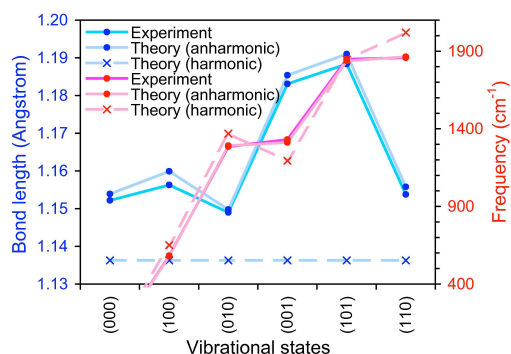
ηr_{12}), an F12-CC method with the aug-cc-pVTZ basis set can achieve equivalent accuracy as the CC method of the same rank with the aug-cc-pV5Z basis set.[6] Combining these F12-CC methods with the grid-based HF equation solver,[1] the exact solutions (eigenvalues) of the Schrödinger equations of neon, boron hydride, hydrogen fluoride, and water at their equilibrium geometries have been obtained as -128.9377 ± 0.0004, -25.2892 ± 0.0002, -100.459 ± 0.001, and -76.437 ± 0.003 E_h, respectively,[10] without resorting to a complete-basis-set extrapolation (**Fig. 2**). They or the corresponding correlation energies agree excellently with other high-accuracy calculations[44-47] or experimental data,[48,49] when available.

1.6. Research Highlights II. Vibrations

Anharmonic vibrational frequencies and vibrationally averaged NMR and structural parameters of FHF⁻.[5] The bifluoride ion (FHF⁻)[50] has the strongest known hydrogen bond[51-53] and is also the only example in which the NMR indirect spin-spin coupling constant across a hydrogen bond is reported.[54] The coupling constants depend sensitively on atom-atom distances and are hence an important probe for structural biology. Understanding the effect of anharmonic vibrations of hydrogen bonds on the structures and spin-spin coupling[55-57] is therefore of fundamental importance in chemistry and biology. We have computed anharmonic vibrational frequencies of FHF⁻ with the vibrational self-consistent-field (VSCF),[58-60] configuration-interaction (VCI),[61] and second-order perturbation (VMP2)[62,63] methods with a multiresolution composite potential energy surface (PES)[64] generated by electronic CCSD(T) method. Anharmonic vibrational averaging has been performed for structures and spin-spin coupling constants, the latter computed by the EOM-CCSD method.[65] The calculations placed the vibrational frequencies at 580 (v_1),

Fig. 3. Anharmonic effects on bond lengths and frequencies as a function of vibrational states.

1292 (v_2), and 1313 (v_3) cm⁻¹, the zero-point H–F bond length (r_0) at 1.1539 Å, the zero-point spin-spin coupling constant [$^1J_0$(HF)] at 124 Hz, and the bond dissociation energy (D_0) at 43.3 kcal/mol. They agree excellently with the observed: 583 (v_1), 1286 (v_2), 1331 (v_3) cm⁻¹,[66] $r_0 = 1.1522$ Å,[66] $^1J_0$(HF) = 124 ± 3 Hz,[54] and $D_0 = 44.4 \pm 1.6$ kcal/mol.[53] The vibrational averaged bond lengths are found to match closely the experimental values of five vibrational states, furnishing a highly dependable basis for correct band assignments (**Fig. 3**). Our calculations have predicted a value of 186 Hz for experimentally inaccessible $^2J_0$(FF).
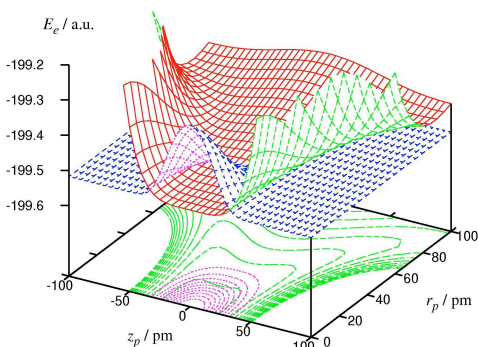
Anharmonic vibrational frequencies and vibrationally averaged structures of hydrocarbon combustion species.[12] The PES's of HCO⁺, HCO, HNO, HOO, HOO⁻, CH₃⁺, and CH₃ in their complete-correlation, complete-basis-set limits have been determined by a combination of CCSD, CCSD(2)$_T$,[43] and CCSD(2)$_{TQ}$ (Ref. 43) and a series of correlation-consistent basis sets.[67-71] A new, compact mathematical representation of PES's has been proposed that hybridizes a fourth-order Taylor expansion and numerical values on a Gauss–Hermite grid. The vibrational frequencies predicted by VCI are typically within 11 cm⁻¹ of the observed (**Fig. 4**).

Molecule	Method	v_1	v_2	v_3	v_4
HCO⁺	Calc.	3083	823	2175	
	Obs.	3089	830	2184	
HCO	Calc.	2432	1079	1874	
	Obs.	2434	1081	1868	
HNO	Calc.	2683	1503	1572	
	Obs.	2684	1501	1565	
HOO	Calc.	3447	1399	1121	
	Obs.	3436	1392	1098	
HOO⁻	Calc.	3587	1088	739	
	Obs.	…	…	775	
CH₃⁺	Calc.	2940	1383	3096	1384
	Obs.	…	1359	3108	1370
CH₃	Calc.	3002	565	3139	1377
	Obs.	3004	606	3161	1400

Fig. 4. Fundamental vibrational frequencies of combustion species.

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Anharmonic vibrational analysis of the guanine–cytosine base pair.[13] The origin of the broad features in the 2800–3800-cm^{-1} region of the infrared spectra[72] of the guanine–cytosine (GC) base pair remains a mystery. Unraveling this is crucial in understanding the ultrafast relaxation (< 100 fs) of the NH stretching vibrational energy that is believed to help protect DNA from UV damage. We have performed a full 81 dimensional anharmonic vibrational analysis using an *ab initio* PES. A strong vibrational resonance among fundamentals of intermolecular NH stretching modes (red-shifted by hydrogen bonds) and various overtones and combinations of fingerprint modes has been shown to be responsible for the observed phenomena.

The nature of the Born–Oppenheimer approximation.[17] In 2006, Takahashi and Takatsuka[73] drew a stunning conclusion about the nature of the Born–Oppenheimer (BO) approximation that the errors due to this approximation scale as $(m/M)^{3/2}$ of the mass ratio of light to heavy particles (m/M). We have revisited this problem by taking as examples the anharmonic vibrations of the linear heavy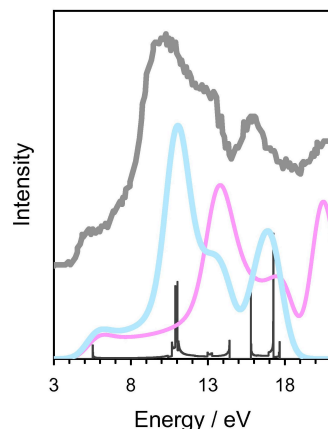–light–heavy molecules such as FHF$^-$, ClHCl$^-$, and BrHBr$^-$. We have compared the energies of the vibrational states obtained with and without the BO separation between the heavy and light nuclei motion. The vibrational Schrödinger equations have been solved on a rectilinear grid in cylindrical coordinates using finite-difference formulas for first and second derivatives (**Fig. 5**). From the numerical results as well as from a mathematical analysis, we have concluded that the previous finding of Takahashi and Takatsuka is not correct. The correct scaling of the errors should be (m/M) and they reduce to $(m/M)^{3/2}$ and $(m/M)^2$, respectively, when the so-called diagonal BO correction is made either perturbatively or variationally.

Fig. 5. Proton wave function (blue/purple) and PES (red/green) in FHF$^-$ in the cylindrical coordinates.

1.7. Research Highlights III. Polymers and Solids

Brillouin-zone downsampling: the modulo MP2 method.[14,16] The cost of an MP2 crystal orbital (CO) calculation[74-94] on a one-dimensional extended system (e.g., polymer) exhibits steep cubic dependence on the number of wave vector (k vector) sampling points in the Brillouin zone (BZ). Reducing this number (K) as much as possible is the key to making MP2 routinely applicable to solids. The validity and accuracy of various ways of reducing K has been investigated. We have proposed the mod-n scheme in which the k vectors are downsampled by a factor of n only in the MP2 step, holding fixed the number of k vectors in the HF step. In one variant of this, the correlation energies of polyethylene and polyacetylene are recovered within 1% of converged values at less than a tenth of usual computational cost.[14] The quasi-particle energy bands have also been reproduced quantitatively with the same approximation. In the most drastic approximation, in which only the Γ point is sampled (the Γ approximation), the correlation energies are recovered within 10% of the converged values with a speedup by a factor of 80–100.[14] The photoelectron spectra of *trans*- and *cis*-polyacetylenes, polyethylene, and polydiacetylene have been reproduced[16] accurately or predicted by MP2 with this scheme (**Fig. 6**).

Fig. 6. Photoelectron spectra of *trans*-polyacetylene. Grey curves: experiment; red curves: HF/6-31G*; blue curves: MP2/6-31G*; histogram: MP2 density of states.

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Explicitly correlated MP2 for extended systems.[20] The formalism of the F12-MP2 method[37] employing basis functions that depend explicitly on the interelectornic distances (r_{12}) has been derived and implemented for extended systems of one-dimensional periodicity. The excitation amplitudes on the r_{12}-dependent factor have been held fixed at values that satisfy the first-order cusp condition.[95] High-rank molecular integrals over Gaussian functions of the r_{12}-dependent factor have been evaluated with the aid of the resolution-of-the-identify approximation[41] and a complementary auxiliary basis set.[42] These integrals and the resulting correlation energy are shown to have the correct size dependence. The F12-MP2 method has been applied to polyethylene, yielding a near-complete-basis-set limit of valence MP2 correlation energy of an extended system for the first time.

Fast correlated methods for molecular crystals: solid formic acid.[7] A high-accuracy electron-correlation ("binary-interaction"[2,96]) method for the routine first-principles determination of energies, structures, and phonon dispersion of molecular crystals has been proposed. It approximates the total energy per unit cell of a crystal by a sum of monomer and overlapping dimer energies in an embedding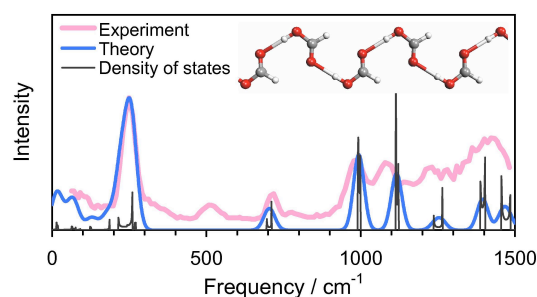 field of self-consistent (therefore, polarizable) atomic charges or dipole moments. First and second energy derivatives with respect to atom positions and lattice constants (useful for characterizing structures and phonons) can be obtained analytically. The method at the MP2 and CCSD levels has been applied to solid formic acid, which is of interest in relation to the structure of hydrogen-bonded solid, liquid, and aerosols,[97] phase transitions,[98] polymorphism,[99-101] concerted proton transfer, etc. Accurate energies with basis set superposition error (BSSE's) corrections, structural parameters, and frequencies and reliable assignments of infrared, Raman, and inelastic neutron scattering spectral bands have been obtained for three conformers (α, β_1, and β_2) of the one-dimensional chains. The results suggest that the observed diffraction and spectroscopic data are consistent with the pristine β_1 form (**Fig. 7**) and that the mysterious infrared band splitting[102] can be assigned to the in-phase and out-of-phase vibrations of adjacent formic acid molecules rather than to the speculated polymorphism.[99-101] Spectral features expected from the α, and β_2 forms have also been shown to be incompatible with the observed Raman[103] and inelastic neutron scattering[104] in the low-energy region.

Fig. 7. Inelastic neutron scattering from solid formic acid in the β_1 form.

Fast correlated methods for molecular crystals: solid hydrogen fluoride.[11] The method described in the previous paragraph has been applied to an infinitely extended chain of hydrogen fluoride at the MP2, CCSD, and CCSD(T) levels with the BSSE correction. The predicted geometries have been in quantitative agreement with the diffraction data.[105] The calculated frequencies are in excellent agreement with the observed[106,107] when and only when both high-level electron-correlation and anharmonic effects (at least within the Γ approximation) are included (**Fig. 8**). The bands in the observed inelastic neutron scattering[108] from solid hydrogen fluoride have also been assigned to the peaks in the calculated phonon density of states.
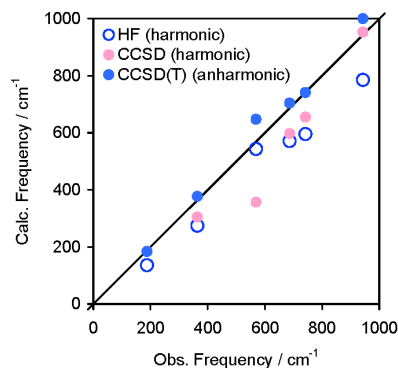

Fig. 8. Calculated and observed frequencies of solid hydrogen fluoride.

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