V-L Development of Model Core Potentials and Post Hartree-Fock Calculations to Atoms and Molecules

We have developed various types of model core potentials for various elements and applied the MCPs to investigate the electronic structures of atoms, molecules, and clusters at levels of post Hartree-Fock calculations. We also investigaed the electronic and vibrational structures of molecules using basis functions for all electrons.

V-L-1 A Theoretical Study on the Ionization of CO_2 and CS_2 with Analysis of the Vibrational Structure of the Photoelectron Spectra

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[*J. Chem. Phys.* **112**, 10838 (2000)]

We have studied the vibrational eigenfunctions, the Frank-Condon factors (FCFs), and the theoretical intensity curves of the four ionic states ($^2\Pi_g$, $^2\Pi_u$, $^2\Sigma_u{}^+$, and $^2\Sigma_g{}^+$) of CO_2 and CS_2 by explicit vibrational calculations using the global region of the potential energy (PE) surface at the MRSDCI level.

The theoretical intensity curves reproduce well the PE spectra. An assignment of the vibrational structures agrees in most cases with that obtained by Turner *et al.*

For the first ionic state ($^2\Pi_g$) of CO_2, the vibrational excitations of the antisymmetric stretching mode should be observed. This situation is connected with the fact that the difference of the vibrational frequencies of the antisymmetric stretching mode between the final and initial states is large. The difference between the two is 1063 cm^{-1}. The FCFs of the (0 0 2) and (1 0 2) transitions are 0.013 and 0.005, respectively. For the first ionic state ($^2\Pi_g$) of CS_2, the difference of the two is 220 cm^{-1}, which is a fifth of that for CO_2. The FCF of the (0 0 2) transition is 0.002.

The spectra of the second ionic states ($^2\Pi_u$) of CO_2 and CS_2 have broad features compared with the other states. This is attributed to the large change (~0.06 Å) in the bond length upon ionization. The change of the $^2\Pi_u$ state is more than three times as large as that of the other states.

V-L-2 A Theoretical Study on the Ionization of OCS with Analysis of the Vibrational Structure of the Photoelectron Spectrum

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[*Theor. Chem. Acc.* submitted]

We have studied the vibrational eigenfunctions, the Frank-Condon factors (FCFs), and the theoretical intensity curves of the four ionic states ($1^2\Pi$, $2^2\Pi$, $1^2\Sigma^+$, and $2^2\Sigma^+$) of OCS by explicit vibrational calculations using the global region of the potential energy (PE) surface at the MRSDCI level.

The theoretical intensity curves reproduce well the PE spectrum except for the spin-orbit splitting. The present calculation supports the assignment of the vibrational structures obtained by Turner *et al.* Delwiche *et al.* have reported the more resolved PE spectrum. An assignment of the vibrational structures is almost consistent with their assignment.

The present calculation proposes the following additional assignment: For the fourth peak of the first ionic state, the (3 0) transition also contributes to intensity in addition to the (0 1) transition. The weak peak at 18.6 eV of the fourth ionic state should be assigned to the (1 2) transition.

V-L-3 Configuration Interaction Study of Differential Correlation Energies in Ca^+, Ca and Ca^-

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[*Phys. Rev. A* **62**, in press (2000)]

Configuration interaction (CI) calculations have been carried out for Ca^+ (4s ^2S, 3d ^2D and 4p $^2P^o$), Ca ($4s^2$ ^1S and 3d4s ^1D) and Ca^- ($4s^24p$ $^2P^o$) using very large Slate-type orbitals. The effect of Ar-like core was included by allowing the excitation from the most important subshells of the core, 3s and 3p, explicitly. A series of multi-reference single and double excitation CI calculations was performed adding important configurations representing valence correlation to the reference space, and convergence of CI energies and wavefunctions was investigated. Valence correlation can be described adequately only when the reference space is expanded so largely that valence correlation is almost completely described by reference functions alone. The relativistic effects were estimated by carrying out Dirac-Fock calculations. The present calculations gave the ionization potentials to 4s ^2S, 3d ^2D and 4p $^2P^o$ to be 6.079, 7.819 and 9.179 eV, respectively, and the excitation energy to 3d4s ^1D to be 2.805 eV. All these calculated values are in good agreement with the observed values. The electron affinity was obtained to be 17.7 meV, which is in excellent agreement with the recent observed values, 17.5 ~ 21.5 meV.

V-L-4 Spin-Orbit Configuration Interaction Calculations of Low-Lying Electronic States of NaCl Using Model Core Potential

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We performed spin-orbit CI calculations for the low-lying $\Omega = 0^+$ states of the NaI molecule in the framework of the model core potentail (MCP) method.

For the I atom, we used scalar relativistic dsp-MCP and (8s/7p/6d) basis set augmented with one diffuse s- and p-type GTFs and two d- and f-type polarization GTFs, resulting in (6111/5111/5111/11). For the Na atom, we used all-electron (533/5) augmented with two p- and d-type polarization GTFs, resulting in (521111/4111/11). The spin-orbit term was calculated in the follwing form:

$$V_{SO,nl}^{mcp}(r) = \lambda \sum_i \frac{B_i \exp(-\beta_i r^2)}{r^2}$$

where λ is a scaling factor.

The potential energy curve of the $A^1\Sigma^+$ state calculated at spin-free scalar relativistic treatment (quasi-relativistic calculation including only mass-velocity and Dawin terms) is almost the same as those given by previous MO calculations but the potential energy curve of the first excited $A0^+$ state calculated at spin-orbit CI treatment is almost the same as those given from the data of previous experiments. The first excited $A0^+$ state has a weight (80%) of the covalent $^3\Pi$ state and 20% of the covalent $A^1\Sigma^+$ state around the ground state equilibrium distance. Thus, the state can be a dipole-allowed transition state with a large transition probability from the ionic ground $X^1\Sigma^+$ state.

V-M Theoretical Study of the Electronic Structures of Weakly Bound Molecules

The electronic structures of weakly bound molecules such as van der Waals molecules are investigated by using sophisticated methods for electronic states, *i.e.*, multi-reference single and double excitation configuration interaction (MRSDCI) and multi-reference coupled pair approximation (MRCPA) calculations.

V-M-1 *Ab initio* Molecular Orbital Study of $Fe(CO)_n$ (n = 1, 2, and 3)

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[*Theor. Chem. Acc.* **104**, 140 (2000)]

Various unsaturated iron carbonyl complexes $Fe(CO)_n$ (n = 1 to 4) have been produced by the UV photolysis of iron pentacarbonyl $Fe(CO)_5$. Among them the spectroscopic studies of the FeCO radical has been extensively performed from both experimental and theoretical points of view and there have been a few experimental spectroscopic constants of $Fe(CO)_2$ and $Fe(CO)_3$.

Although there have been published several theoretical studies for $Fe(CO)_2$ and $Fe(CO)_3$, there are few comprehensive studies for the change of bonding nature in the $Fe(CO)_n$ (n = 1 to 3) radicals. In this study we have carried out MCSCF calculations for the $Fe(CO)_n$ (n = 1 to 3) to investigate the nature of bonding respect to change in the number of CO ligands. The calculated bond lengths of R(Fe–C) are reasonably in agreement with experimental values and more sophisticated theoretical results. From the Mulliken population analysis, the traditional donation and back donation mechanism is valid for FeCO through $Fe(CO)_3$.

V-M-2 *Ab initio* CASSCF and MRSDCI Calculations of the $(C_6H_6)_3^+$ Radical

MIYOSHI, Eisaku; GHOSH, Tapas Kumar

[*Chem. Phys. Lett.* **323**, 434 (2000)]

Ab initio complete active space self-consistent-field (CASSCF), single-reference singly and doubly excited configuration interaction (SRSDCI), and multi-reference SDCI (MRSDCI) calculations were performed for the benzene trimer cation radical, $(C_6H_6)_3^+$, in the ground state. We obtained the equilibrium geometry of the D_{6h} sandwich structure and found that the global minimum of the cation is at the distorted C_{2v} sandwich structures. This minimum is 0.032 eV lower than that of the D_{6h} sandwich structure. The dissociation energy (D_e) relative to $(C_6H_6)_2^+ + C_6H_6$ was calculated to be 0.43 eV, in comparison to the experimental value (D_0) of 0.34 ± 0.02 eV. Our calculations suggest that the bands observed by Nishi and co-workers at 1.02 and 1.29 eV can both be assigned to the split components of the $^2E_{1u}$ state, which are charge resonance states. This is also the case for the benzene dimer cation radical. In the ground state of the trimer cation radical, almost all the charge is localized at the central benzene ring, which has a gross charge of +0.9. This observation contrasts with speculations by experimentalists that the charge is localized in the dimer core or delocalized over all three benzene rings.

V-M-3 Molecular Orbital Study on OH Stretching Frequency of Phenol Dimer and its Cation

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Ab initio calculations were performed to investigate the structure and bonding of the phenol dimer and its cation, especially, the OH stretching frequencies. Some stable structures of the phenol dimer and its cation were obtained at the Hartree-Fock level and were found in agreement with predictions based on spectroscopic investigations. In these dimers the phenol moieties are bound by a single OH··O hydrogen bond. The hydrogen bond is much stronger in the dimer cation than in the neutral dimer. The calculated binding energy of the phenol dimer in the most stable structure was 6.5 ~ 9.9 kcal/mol at various levels of calculation compared with the experimental value of ≥ 5 kcal/mol. The binding energy of the phenol dimer cation is more than three times (24.1 ~ 30.6 kcal/mol) as large as that of the neutral dimer. For the phenol dimer the OH stretching frequency of the proton accepting phenol (PAP) is 3652 cm^{-1} and that of the proton donating phenol (PDP) is 3516 cm^{-1}; these are in agreement with observed values of 3654 cm^{-1} and 3530 cm^{-1}, respectively. For the phenol dimer cation the OH stretching frequency of the PAP is 3616 ~ 3618 cm^{-1} in comparison with an observed value of 3620 ± 3 cm^{-1}. That of the PDP in the dimer cation is calculated to be 2434 ~ 2447 cm^{-1}, which is 1210 ~ 1223 cm^{-1} smaller than that of the bare phenol. The large reduction of the OH stretching frequency of the PDP in the phenol dimer cation is attributed to the formation of a stronger hydrogen bond in the cation than in the neutral dimer.

V-N Theory for Quantum Liquids and Molecular Dynamics Study Using Potentials by *ab initio* Molecular Orbital Calculations

We derived generalized Ornstein-Zernike equations for quantum liquids. The set of equations can be applicable to homogeneous and isotropic Bose and Fermi liquids such as ^{3}He, ^{4}He, and electron liquids at arbitrary temperature. Using potentials obtained by ab initio molecular orbital calculations, molecular dynamics calculations were also performed to investigate physical properties of liquid mercury.

V-N-1 An Integral Equation Theory for Quantum Liquids: Finite-Temperature Kohn-Sham Debsity-Functional Formulation

SUMI, Tomonari; SATO, Hirofumi; HIRATA, Fumio; MIYOSHI, Eisaku

[*Phys. Rev. E* submitted]

We derived a generalized Ornstein-Zernike equation for quantum liquids, where the uncertainty in particle position is considered by using a self-correlation function for an ideal quantum liquid. To determine a self-consistent solution of the finite-temperature Kohn-Sham equation introduced by Chihara [*Prog. Theor. Phys.* **50**, 1156 (1973)] combined with the generalized Ornstein-Zernike equation for quantum liquids, we present two types of closure relation. One is obtained by extending Percus' method for quantum liquids, and the other is derived from the nonlinear Debye-H_ckel approximation. These sets of equations can be used to determine the pair correlation function and the direct correlation function for homogeneous and isotropic Bose and Fermi liquids.

V-N-2 Structure Change of Supercritical Mercury

SUMI, Tomonari; MIYOSHI, Eisaku

It has been well known that density fluctuations and correlation lengths which are related to the long-range structure of liquids have maxima in the supercritical region. Morita *et al.* found by using small-angle X-ray scattering experiments that the maxima for supercritical water, CO_2, and CF_3H are in a little lower density region than the critial isochore.1) They also estimated the density fluctuations and correlation lengths of Hg by using the equations of state and showed that the maxima are in the lower density region from the critical isochore and the deviations become larger with increasing temperature.

We have performed molecular-dynamics (MD) calculations for liquid mercury in the regions including the metal-nonmetal transition region under pair-potential approximation using the potential energy curve of the dimeric Hg, and showed that the pair-potential approximation gives a good qualitative description of the metallic interatomic force for liquid mercury and MD calculations using this approximation demonstrate the characteristic change of force fields between liqiud metal and liquid semiconductor.2) In the present study, we performed MD calculations for superdritical mercury under fixed pressures and discussed the relationship between fluctuations of the long-range structure and the change of the local structure.

The density dependence of the first peak of the pair distribution function were examined for supercritical mercury under a fixed pressure, showing that the peak shifts to longer distance with decreasing density, while the peak height has minimum at a density. This change is due to a crossover from shorter distance between the nearest neighboring atoms in liquid phase to longer distance in gas phase. It can be easily considered that the fluctuations of local structure become large near the crossover region.

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