

## V-M 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.

### V-M-1 Theoretical Study of Low-Lying Electronic States of TiCl and ZrCl

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Low-lying electronic states of TiCl and ZrCl were investigated by the complete active space SCF (CASSCF), multi-reference singly and doubly excited configuration interaction (MRSDCI), and multi-reference coupled pair approximation (MRCPA) calculations using the model core potential (MCP) method. The relativistic effects were incorporated in the MCP and basis sets for Zr at the level of Cowan and Griffin's quasirelativistic Hartree Fock method. The  $^4\Phi$  state was found to be the ground state of TiCl whereas the  $^2\Delta$  state was the ground state of ZrCl at all levels of calculations. Two low-lying excited states were very close in energy to the ground state. The excited  $^4\Sigma^-$  and  $^2\Delta$  states of TiCl were higher than the ground state by 0.102 eV and 0.458 eV, respectively, and the excited  $^4\Phi$  and  $^4\Sigma^-$  states of ZrCl were higher by 0.094 eV and 0.110 eV, respectively, at the MRCPA calculations.

### V-M-2 Benchmarking of Model Core Potentials: Application to the Group 4 Metal Halogen Complexes (MX<sub>4</sub>: M = Ti, Zr, Hf and X = F, Cl, Br, I)

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The reliability of the model core potential method was probed in a systematic study of the group 4 metal halogen complexes (MX<sub>4</sub>; M = Ti, Zr, Hf and X = F, Cl, Br, I). In the first phase of the study we focused on the geometries of these tetrahedral complexes. The computed M-X distances were compared with experimental values, as well as those predicted using a variety of effective core potentials. The reaction energies for a

simple set of halogen diatomic substitution reactions of the MX<sub>4</sub> complexes leading to the mixed halogen complex, MX<sub>2</sub>Y<sub>2</sub>, were studied in the second part of this work. Although no experimental values are available for these reactions, comparison was again made with the values computed using a number of effective core potential methods. All of the calculations were carried out at the RHF and MP2 levels of theory. Discussion focuses on the predictability of the different pseudopotential techniques and the extent of the metal atom valence space. Furthermore, we comment on the importance of the metal atom valence basis set contraction scheme and polarization space.

### V-M-3 Configuration Interaction Study of Differential Correlation Energies in Ca<sup>+</sup>, Ca and Ca<sup>-</sup>

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Configuration interaction (CI) calculations have been carried out for Ca<sup>+</sup> (4s <sup>2</sup>S, 3d <sup>2</sup>D and 4p <sup>2</sup>P<sup>o</sup>), Ca (4s<sup>2</sup> <sup>1</sup>S and 3d4s <sup>1</sup>D) and Ca<sup>-</sup> (4s<sup>2</sup>4p <sup>2</sup>P<sup>o</sup>) 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 <sup>2</sup>S, 3d <sup>2</sup>D and 4p <sup>2</sup>P<sup>o</sup> to be 6.079, 7.819 and 9.179 eV, respectively, and the excitation energy to 3d4s <sup>1</sup>D 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.

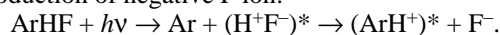
## V-N Theoretical Study of the Electronic Structures of Weakly Bound Molecules

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-N-1 *Ab initio* Study of the van der Waals Molecule ArHF**

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*Ab initio* calculations were performed for the van der Waals complex ArHF using the multi-reference single and double excitation configuration interaction (MRSDCI) and multi-reference coupled pair approximation (MRCPA) methods to determine the spectroscopic parameters and potential energy surfaces of the ground X <sup>1</sup>Σ<sup>+</sup> and first excited 2<sup>1</sup>Σ<sup>+</sup> states. The calculated ground-state equilibrium constants compared well with the available data. This is the first report of spectroscopic data for the excited state. Another subject of this study was the possibility of a fluorine anion from an excited ionic state (ArHF)<sup>\*</sup> produced by Ar colliding with an excited ionic state of HF. The excited 2<sup>1</sup>Σ<sup>+</sup> state is of ionic type (H<sup>+</sup>F<sup>-</sup>) and dissociates to a negative fluorine ion. This enlightens the photochemical reaction of the ionic excited HF with Ar correlating to the production of negative F ion:

**V-N-2 *Ab initio* Molecular Orbital Study of Fe(CO)<sub>n</sub> (n = 1, 2 and 3)**

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Various unsaturated iron carbonyl complexes Fe(CO)<sub>n</sub> (n = 1 to 4) have been produced by the UV photolysis of iron pentacarbonyl Fe(CO)<sub>5</sub>.<sup>1</sup> 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)<sub>2</sub> and Fe(CO)<sub>3</sub>.

Although there have been published several theoretical studies for Fe(CO)<sub>2</sub> and Fe(CO)<sub>3</sub>, there are few comprehensive studies for the change of bonding nature in the Fe(CO)<sub>n</sub> (n = 1 to 3) radicals. In this study we have carried out MCSCF calculations for the Fe(CO)<sub>n</sub> (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)<sub>3</sub>.

**Reference**

1) K. Tanaka, K. Sakaguchi and T. Tanaka, *J. Chem. Phys.* **106**, 2118 (1997).

**V-N-3 *Ab initio* Study on the Ground State of the C<sub>3</sub>O<sub>2</sub> Molecule**

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Restricted Hartree-Fock (RHF) and single-reference coupled pair approximation (SRCPA) calculations were performed for the ground state of the C<sub>3</sub>O<sub>2</sub> molecule. The SRCPA calculations revealed that C<sub>3</sub>O<sub>2</sub> is quasi-linear with a global minimum in a W-shaped structure (C<sub>2v</sub> symmetry) with ∠C-C-C = 153.6° and ∠C-C-O = 176.4°. To obtain the qualitatively correct description that the C<sub>3</sub>O<sub>2</sub> molecule has a global minimum in the W-shaped structure, basis sets of higher quality than double-zeta with double polarization functions are indispensable. The observed very low frequency of 18.2 cm<sup>-1</sup> is not a fundamental vibrational frequency along the ν<sub>7</sub> mode, but should rather be assigned to the transition between two vibrational states which are split by the interaction of two ground vibrational state in the double minima.

**V-N-4 On the Calculation of Binding Energy of the (C<sub>6</sub>H<sub>6</sub>)<sup>3+</sup> Ion**

**GHOSH, Tapas Kumar; MIYOSHI, Eisaku**

The benzene trimer cation, (C<sub>6</sub>H<sub>6</sub>)<sup>3+</sup>, has become an important system in the cluster ion spectroscopy because of the identification of core in the ion. It is yet controversial whether the benzene trimer cation has charge delocalized or localized structure. We performed *ab initio* CASSCF followed by MRSDCI as well as SRSDCI calculations for the benzene trimer cation (C<sub>6</sub>H<sub>6</sub>)<sup>3+</sup> in its ground state assuming a sandwich-like structure. The total number of generated CSFs in MRSDCI calculations was 7,131,105. The equilibrium distances between two consecutive rings at the global minimum of the trimer cation in its ground state calculated by CASSCF in C<sub>2v</sub> symmetry were 7.299 a.u. The dissociation energy (D<sub>e</sub>) for the ground state of benzene trimer cation relative to (C<sub>6</sub>H<sub>6</sub>)<sup>2+</sup> + C<sub>6</sub>H<sub>6</sub> was calculated to be 195 meV at the CASSCF level and 349 meV at the MRSDCI including Davidson's correction in comparison to the experimental value (D<sub>0</sub>) of 338 meV. The total binding energy relative to 2C<sub>6</sub>H<sub>6</sub> + C<sub>6</sub>H<sub>6</sub><sup>+</sup> was calculated to be 757 meV at the MCSCF level and 984 meV at the MRSDCI including Davidson's correction, which is in agreement with a recent experimental upper limit of 990 ± 50 meV. It has been concluded from our calculation that in the trimer cation charge is localized at the central benzene ring, not that the charge is localized on a dimer core as was suggested by some experimentalists.

## V-O Molecular Dynamics Study Using Potentials by *ab initio* Molecular Orbital Calculations

Using potentials obtained by *ab initio* molecular orbital calculations, molecular dynamics calculations were performed to investigate physical properties of liquid mercury.

### V-O-1 Molecular Dynamics Study of Liquid Mercury in the Density Region between Metal and Nonmetal

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[*Phys. Rev. B* **59**, 6153 (1999)]

We performed SDCI, SDCI(+Q), and CPA calculations for the ground  $^1\Sigma_g^+$  state of  $\text{Hg}_2$  incorporating the 5d and 6s electron correlations and major relativistic effects. The many-electron-excitation effect produces spectroscopic constants close to the experimental values. Although the metal-nonmetal (M-NM) transition can be explained as a simple band-crossing transition in one-electron theory, the many-electron-excitation effect is very important for describing the interaction between mercury atoms.

MD calculations for expanded liquid mercury were performed using the potential energy curve of  $\text{Hg}_2$ , in the regions including the M-NM transition range. The volume ( $V$ ) dependence of the thermal pressure coefficient,  $\gamma_v$ , and the internal pressure,  $P_0$ , estimated by the MD calculations agree well with experimental results. Thus, many-body interactions or the qualitative change in the form of interatomic interactions arising from density dependence are not necessarily essential to explain the behavior of the  $\gamma_v$  vs.  $V$  and the  $P_0$  vs.  $V$  curves. The change of calculated pair distribution function between metallic and nonmetallic state qualitatively demonstrates the change of experimental ones. The temperature dependence of the isochoric electrical conductivity was estimated using interatomic distances obtained from the calculated pair distribution functions. It was shown that the increase of the isochoric electrical conductivity accompanying an increase in temperature can be realized through the increase of the density of states at the Fermi energy. In the preceding paper,<sup>1)</sup> we reported that the MD calculations near the melting point using the potential curve of  $\text{Hg}_2$  reproduce the cooperative motion corresponding to the collective short-wavelength excitations in the dynamic structure factor. These results suggest that pair-potential approximation using the potential curve of the dimeric molecule 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 liquid metal and liquid semiconductor. However, the both  $\gamma_v$  vs.  $V$  and  $P_0$  vs.  $V$  curves estimated by the MD calculations seem to deviate from the observed values slightly in the high-density metallic region. These differences between the observed and calculated values may be attributed to the lack of the many-body effects.

It has been pointed out<sup>2)</sup> that the relative importance

of three-body interactions compared with two-body interactions in the liquid-vapor critical range for mercury is larger than for other van der Waals molecules. The boiling point determined by the present MD calculations is much higher than the observed value. This higher temperature should be corrected by considering three-body effects, such as the Axilrod-Teller interaction, because the three-body dispersion forces are repulsive while the two-body dispersion force is a long-range attractive force. It is interesting to determine the liquid-vapor coexistence curve with pair-potential approximation using the potential energy curve of  $\text{Hg}_2$  and to investigate the contribution of three-body effects to the liquid-vapor transition phenomena, especially in liquid-vapor critical range.

#### References

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- 2) M. W. Pestak, R. E. Goldstein, M. W. Chan, J. R. de Bruyn, D. A. Balzarini and N. W. Ashcroft, *Phys. Rev. B* **36**, 599 (1987).

### V-O-2 The Liquid-Vapor Coexistence Curves of Fluid Mercury

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It has been known that the liquid-vapor coexistence curve of mercury is different from those of alkali metals (Rb, Cs) and inert gases (Ar, Xe).<sup>1)</sup> The followings have been established for these liquid-vapor coexistence curves and the rectilinear diameters,  $r_d = (r_L + r_V)/2r_c$ , where  $r_L$ ,  $r_V$ , and  $r_c$  is the coexisting liquid density, vapor density, and the critical density, respectively: (1) The two phase region of mercury is narrower than those of alkali metals and inert gases; (2) The  $r_d$  of inert gases is a linear function of temperature,  $T$ , which is the law of rectilinear diameter, except for the near critical point, while the  $r_d$  of alkali metals and mercury deviate from the law of rectilinear diameter in wide temperature region. It has been suggested that the evidence in (2) might be attributed to many body effects.<sup>2)</sup>

We have performed molecular dynamics (MD) calculations for liquid mercury using the potential energy curve of dimeric mercury ( $\text{Hg}_2$ ), which was obtained by molecular orbital calculations, in order to study the properties of mercury at the various temperature and density regions. In particular, the MD calculations using this approximation qualitatively reproduced the volume dependence of the thermal pressure coefficient and the internal pressure in the density regions including the metal-nonmetal transition range.<sup>3)</sup> In this study, the MD calculations of fluid mercury are performed to determine the liquid-vapor phase transition points of mercury, and the relationship between the pair potential and liquid-vapor coexistence

curve is discussed.

The pair potential have been obtained from the CPA calculations developed by Tanaka and co-workers. The MD calculations were performed using a Verlet algorithm with 864 particles in an isothermal and isobaric ensemble with a time step of 0.005 fs. The physical quantities near the transition points were determined from the statistical averages over 2 000 000 to 10 000 000 intervals.

The results of MD calculations are as follows: (1) Our calculations qualitatively reproduced the liquid-vapor coexistence curve of mercury which is mentioned above; (2) Calculated  $r_d$  is not a linear function of  $T$ . Thus, our results suggest that the law of rectilinear diameter breaks down in the pair potential approximation.

#### References

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- 3) T. Sumi, E. Miyoshi and K. Tanaka, *Phys. Rev. B* **59**, 6153 (1999).