developed for the simultaneous determination of Pd(II) and Pt(II) as their cyano complexes. The method provides good sensitivity of *ca.* 2 pg with extremely small quantity of sample (*ca.* 40 µ*l*) as well as simple analytical procedure.

The present CE methodology was applied to a real sample, *e.g.*, anode slime obtained from an electrolytic copper refinary. The analytical data obtained for Pd and Pt were in accord with those obtained independently by the inductively coupled plasma atomic emission spectrometry.

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The LS→HS Transition of Cobalt(III) in an Oxygen Lattice with the K₂NiF₄-Type Structure: Correlations with the Chemical Bonding Environment of the (CoO₆) Octahedron Along the c-axis

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In oxides characterized by the K₂NiF₄-type structure, the low-spin→high-spin transitioin of trivalent cobalt ion was studied in function of the nature of competing bonds in the perovskite-plane and along the c-axis. Using Slichter and Drickamer's model the calculated values of parameters characterizing such a transition are correlated with the covalency of competing bonds along the c-axis of the K₂NiF₄-structure and the local structural distortion of the (CoO₆) octahedron.

Introduction

During last twenty years, a lot of studies involving the spin-state transition in cobalt(III) oxides have been carried out. The first oxygen lattice selected was the three-dimensional perovskite structure $ACoO_3$ (A=rare earth)[1,2], or $A_2M'CoO_6$ (A=Sr, Ba; M'=Sb)[3,4]. The cobalt(III) oxides with the layered structure derived from the K₂NiF₄-type have been also recently investigated[5].

The change of electronic configurations of transition metal ions versus temperature is an interesting phenomenon due to the modifications of the induced magnetic properties. Co-

balt(III) seems to be a good candidate, the low-spin state being characterized by a $^1A_{1g}$ diamagnetic ground term and the high-spin state by a paramagnetic $^5T_{2g}$ one (in O_h symmetry).

The oxides with general formular $(A, A')_2(M, M')O_4$ appeared to be a good model for evaluating the influence of the different chemical bonding factors on the low-spin(LS)→high-spin(HS) transition, the (MO₆) octahedron being surrounded by two types of competing bonds:

−(M'-O) in the perovskite-plane

−[(A, A')-O] along the c-axis (Figure 1).
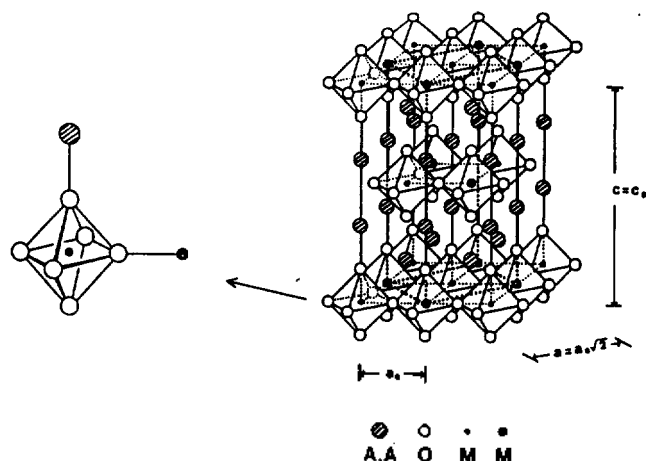
Such competing bonds can anisotropically modify the cova-

Figure 1. K₂NiF₄-type structure and corresponding two types of competing bonds surrounding the (MO₆) octahedron.

Table 1. Unit Cell Parameters of $A'_{0.5}La_{1.5}Zn_{0.5}Co_{0.5}O_4$ (A'=Sr and Ba) Oxides with K₂NiF₄-Type Structure

Compounds	a_0 (Å)	c_0 (Å)	$a_0\sqrt{2}$ (Å)	c_0/a_0	V (Å³)
$Sr_{0.5}La_{1.5}Zn_{0.5}Co_{0.5}O_4$	3.844	12.58	5.346	3.27	185.29
$Ba_{0.5}La_{1.5}Zn_{0.5}Co_{0.5}O_4$	3.877	12.81	5.483	3.30	192.55

lency of the (M-O) bonds of the (MO₆) octahedron. The change of the covalency then induces a modification of the local structure as well as the local crystal-field energy. These variations can be evaluated through various techniques including Mössbauer resonance, electron paramagnetic resonance, nuclear magnetic resonance, and infra-red spectroscopies[6-9] and the Riedveld refinement of X-ray diffraction pattern[10].

In order to correlate the nature of the (M'-O) competing bond in the perovskite-layer to the local structural distortion of the (CoO₆) octahedron, $Sr_{0.5}La_{1.5}M'_{0.5}Co_{0.5}O_4$(M'=Mg and Zn) have been prepared and studied[11]. In such a study, where the competing bonds along the c-axis are not varied, the lower ionicity of the (Zn-O) bond compared with the (Mg-O) one induced a smaller elongation of the (CoO₆) octahedron. Due to the small local elongation of the (CoO₆) octahedron and the strong increase of the effective magnetic moment, only the low-spin (LS; $^1A_{1g}$)→high-spin (HS; $^5T_{2g}$) transition (without consideration of the intermediate spin state ($^3T_{2g}$)) could be discussed for trivalent cobalt ion in these oxides[12,13]. Taking into account all possible additional magnetic contributions to corresponding experimental magnetic susceptibility and using Slichter and Drickamer's model[14], the LS→HS transition have been characterized. Since $^1A_{1g}$ term corresponds to an isotropic electronic configuration ($t_{2g}^6e_g^0$) and the high-spin configuration ($t_{2g}^4e_g^2$) induces only a small anisotropy on filling partially the t_{2g} orbitals, the LS →HS transition was not strongly dependent on the local elongation of the (CoO₆) octahedron.

However, the replacement of A alkaline earth cation would show completely different influence on the spin-state transition of Co(III) because if the difference in covalency of A-O bond is not so large, the large difference in ionic radii of A cations is able to induce strong steric effect[13]. The purpose of the present study, therefore, is to compare the influence of competing chemical bond along the c-axis with that in the perovskite-plane on the spin-state transition of cobalt(III). In order to modify both the covalency and steric effects on such a $^1A_{1g}$→$^5T_{2g}$ transition, $A_{0.5}La_{1.5}Zn_{0.5}Co_{0.5}O_4$ (A=Sr and Ba) were selected.

Preparations

The stoichiometric mixtures of strontium (or barium), zinc, and cobalt nitrates and lanthanium acetate were slowly decomposed in the air and heated at 900 °C for 48 hours under the oxygen flowing conditions. The resulting powders were treated at 850 °C under moderate oxygen pressure (10 MPa) for 24 hours and finally at 800 °C under 1 kbar (0.1 GPa) of oxygen pressure for 24 hours. Particularly in case of $Ba_{0.5}$-$La_{1.5}Zn_{0.5}Co_{0.5}O_4$, the omission of pretreatment under relatively low pressure resulted in the formation of mixed phase containing LaCoO₃ with perovskite structure. A treatment under higher oxygen pressure was required to stabilize 3+ oxidation state of cobalt ion in the lattice.

The oxidation states of cobalt ion in the final products were determined by the iodometric titration (3.02± 0.04 and 3.05± 0.03 for $Sr_{0.5}La_{1.5}Zn_{0.5}Co_{0.5}O_4$ and $Ba_{0.5}La_{1.5}Zn_{0.5}Co_{0.5}O_4$, respectively).

The powder X-ray diffraction patterns of two products could be indexed on the basis of a tetragonal K₂NiF₄-type unit cell with I_4/mmm space group. No extra line was observed in Guinier film of $Ba_{0.5}La_{1.5}Zn_{0.5}Co_{0.5}O_4$. Due to the charge and size difference ($r_{Co(III)}$=0.545 Å, $r_{Zn(II)}$=0.74 Å)[15], however, an 1 : 1 Zn/Co ordering can be expected in the perovskite-layer. Unit cell parameters of two oxides are compared in Table 1. The replacement of strontium (r=1.31 Å) by barium (r=1.47 Å) leads to a large expansion of the c_0 parameter inducing some increase of the c_0/a_0 ratio.

Magnetic Study

The magnetic susceptibilities of $A_{0.5}La_{1.5}Zn_{0.5}Co_{0.5}O_4$ (A=Sr, Ba) phases have been measured from 4.2 to 800 K using a susceptometer DSM 8 in which the torque needed to place the swinging pendulum containing sample at zero position is converted into the induced magnetic moment.

As shown in Figure 2 and 3, the thermal variations of χ'_M^{-1} after the diamagnetic correction illustrate a spin-state transition. On the $\chi'_M^{-1}=f(T)$ curves, maximum values of χ'_M^{-1} are observed at about 300 and 220 K for A=Sr and Ba, respectively, which are not drastically different. Since the thermal variation of effective magnetic moment is too high and the c_0/a_0 ratio too small to involve a contribution of the intermediate $^3B_{2g}(^3T_{2g})$ term[11], the evolution of χ'_M^{-1} vs. T can be associated to a low-spin ($^1A_{1g}$)→high-spin [^5E_g ($^5T_{2g}$)] transition as described in previous works[12,13]. On the same basis developed for the fitting of magnetic curve of $Sr_{0.5}La_{1.5}Zn_{0.5}Co_{0.5}O_4$ oxide, the magnetic susceptibility of $Ba_{0.5}$-$La_{1.5}Zn_{0.5}Co_{0.5}O_4$ phase can be expressed as follows:

$$\chi_M = -100\times10^{-6}+50\times10^{-6}+\frac{0.139}{T+16}$$

$$+\frac{0.0151}{T}\times\frac{15\ \exp(-401/kT)}{1+\exp(-401/kT)}+\frac{0.458}{T}\times C_{Co(III)}Y(T)$$

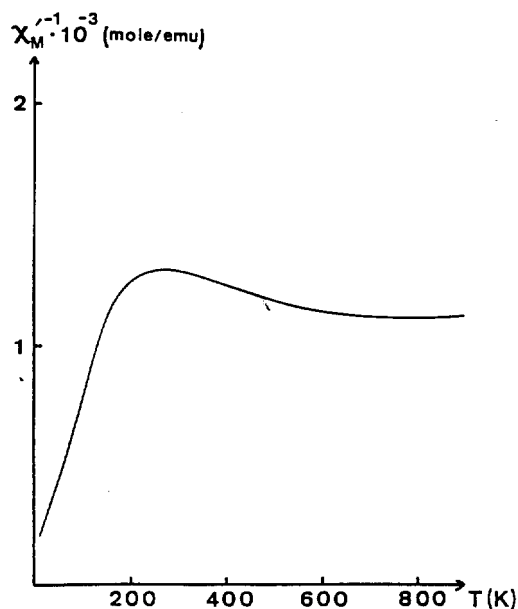$X_M'^{-1} \cdot 10^{-3}$ (mole/emu)

Figure 2. Thermal variation of the reciprocal molar magnetic susceptibility for $Ba_{0.5}La_{1.5}Zn_{0.5}Co_{0.5}O_4$.

$X_M'^{-1} \cdot 10^{-3}$ (mole/emu)

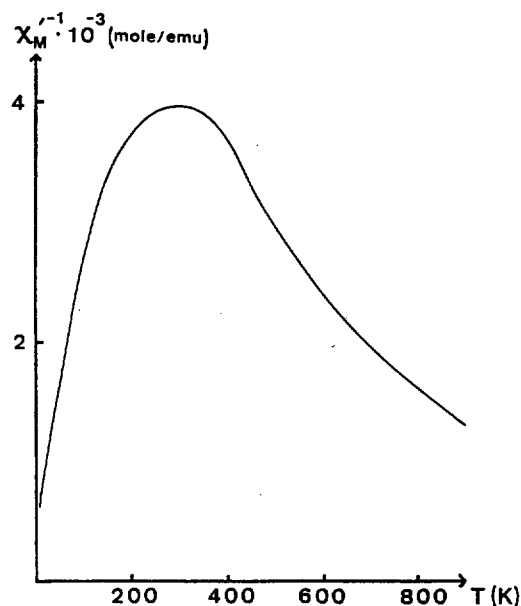**Figure 3.** Thermal variation of the reciprocal molar magnetic susceptibility for $Sr_{0.5}La_{1.5}Zn_{0.5}Co_{0.5}O_4$.

$X_M \cdot 10^4$ $\left(\frac{emu}{mole}\right)$

Figure 4. Thermal variation of the different contributions to the molar magnetic susceptibility of $Ba_{0.5}La_{1.5}Zn_{0.5}Co_{0.5}O_4$.

The first term is a diamagnetic contribution (χ_{diam}) of constituting ions[16].

The second one is the second order van Vleck-type constant paramagnetism $N\alpha$ characterizing 0.5 mole Co(III) ions in the low-spin state ($N\alpha = 8Nk^2\beta^2/10$ Dq). The delocalization factor k was assumed to be 1 and the crystal field parameter 10 Dq estimated as 20,000 cm^{-1} [17].

The third is an impurity term involving the Curie-Weiss type behavior attributed to some high-spin Co(III) ion stabilized by the intrinsic crystal defects such as oxygen vacancies inducing a local decrease of the crystal-field energy. The fitting of magnetic curve between 4.2 and 50 K by the equation ($\chi_M - \chi_{diam} - 0.5N\alpha$)$^{-1}$=$f(T)$ gave the evaluation of Curie-
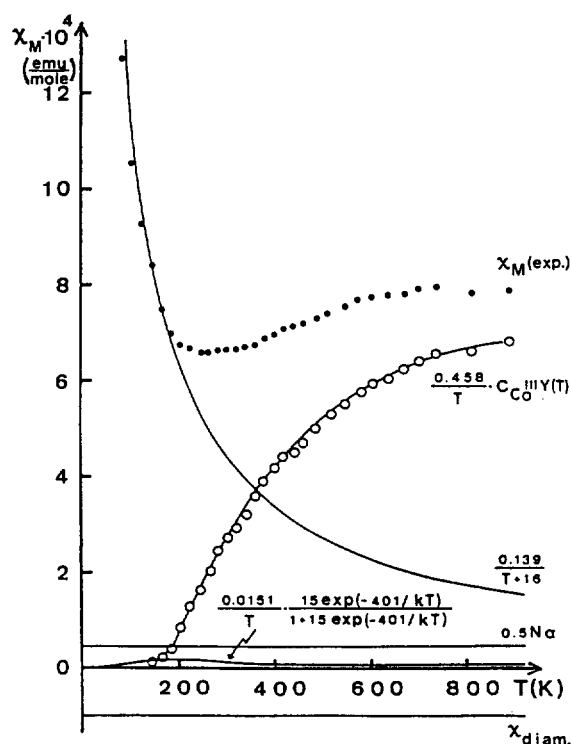
Weiss temperature (-16 K) and Curie constant (0.139) corresponding to 4.11×10^{-2} mole of impurities when Curie constant for the high-spin Co(III) is taken as 3.38[3].

The fourth represents a Boltzmann-type distribution between $^1A_{1g}$ and $^5T_{2g}$ levels of total multiplicities (spin+orbital; 1 and 15, respectively) for high-spin Co(III) cations belonging to the surface[18]. The constants 401 K and 0.0151 corresponding to 1.32×10^{-3} mole were obtained by the fitting of magnetic curve between about 50 and 250 K.

The last characterizes the thermal variation of 0.458 mole of cobalt ions in the bulk per $Ba_{0.5}La_{1.5}Zn_{0.5}Co_{0.5}O_4$. The $Y(T)$ values at corresponding temperatures represent the fraction (x_{HS}) of Co(III) ions with high-spin configuration in the bulk.

Figure 4 shows the thermal evolution of the different magnetic contributions previously described to the experimental molar magnetic susceptibility χ_M of $Ba_{0.5}La_{1.5}Zn_{0.5}Co_{0.5}O_4$. The plot of ln$K$ ($K=x_{HS}/(1-x_{HS})$; the equilibrium constant between low-spin ($^1A_{1g}$) and high-spin ($^5T_{2g}$), where x is the mole fraction in corresponding spin state) versus $1/T$ leads to the evaluation of the energy separation between two spin-states (Figure 5). From the Slichter and Drickamer's model[14], the total free energy of a mixture of low-spin and high-spin species can be expressed by the following equation;

$$G = x_{HS}G_{HS} + (1-x_{HS})G_{LS} + \Gamma x_{HS}(1-x_{HS}) - TS_{mix}.$$

At equilibrium, $(\partial G/\partial x_{HS})_{P, T}=0$ yields

$$\ln K = \ln[x_{HS}/(1-x_{HS})] =$$
$$-[\Delta H^\circ + \Gamma(1-2x_{HS})]/RT + \Delta S^\circ/R$$

The ΔH°, ΔS°, and Γ (an interaction parameter between the neighboring Co(III) ions in the oxygen lattice) describing the spin-state transition can be estimated from Figure 5.
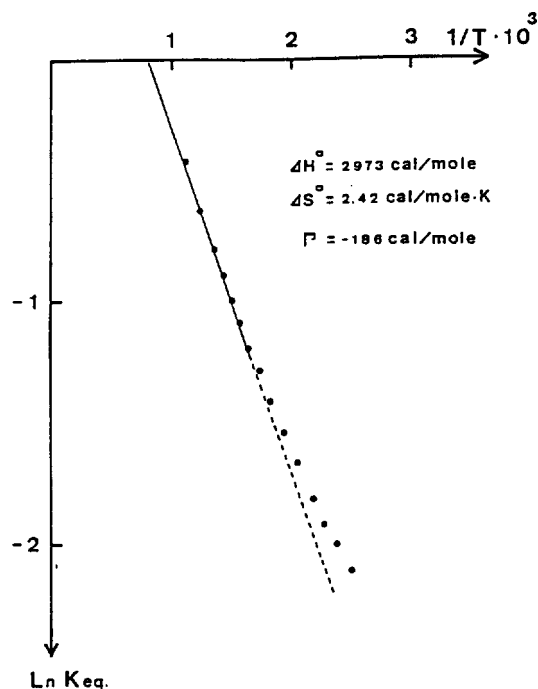
Figure 5. Variation of $\ln K$ vs. $1/T$ for $Ba_{0.5}La_{1.5}Zn_{0.5}Co_{0.5}O_4$.

Table 2. The Temperatures and Thermodynamic Parameters Characterizing the Spin-State Transition of Co(III) Ion in $A'_{0.5}La_{1.5}$ $M'_{0.5}Co_{0.5}O_4$ (A' = Sr, Ba and M' = Mg, Zn)

Compounds	T_i^* (K)	ΔH^o (cal/mole)	ΔS^o (cal/mole·deg)	Γ (cal/mole)
$Sr_{0.5}La_{1.5}Mg_{0.5}Co_{0.5}O_4$	500	6170	4.07	−425
$Sr_{0.5}La_{1.5}Zn_{0.5}Co_{0.5}O_4$	300	4960	3.68	−41
$Ba_{0.5}La_{1.5}Zn_{0.5}Co_{0.5}O_4$	220	2973	2.42	−186

*The spin state transition temperature is referred following Demazeau *et al.* (1)

The values of such parameters of $Ba_{0.5}La_{1.5}Zn_{0.5}Co_{0.5}O_4$ are calculated and compared with those of isostructural $Sr_{0.5}La_{1.5}$ $Mg_{0.5}Co_{0.5}O_4$ and $Sr_{0.5}La_{1.5}Zn_{0.5}Co_{0.5}O_4$ in order to evaluate the influence of chemical bonding along the c-axis as well as perovskite-type plane (Table 2).

Under the same competing condition in the perovskite-plane, two main differences can be observed when the strontium is replaced by the barium: a strong decrease of the ΔH^o value (4960 to 2973 cal/mole). and the modification of Γ value (-41 to -186 cal/mole). The enthalpy change ΔH represents the sum of different terms such as the difference in internal energy ΔU (essentially Madelung energy), the difference in electronic energy ($E_{HS} - E_{LS} = \Delta E$) considered as the energy separation between $^1A_{1g}$ and $^5T_{2g}$ levels, and the difference in vibrational energy of various modes of phonons (Δ_{vib}). The decrease of ΔH^o including above terms is induced by mainly the expansion of the lattice (see Table 1). If we consider only the average covalency of the axial competing bond, a small increase of the local crystal-field strength at the Co(III) site (therefore a small increase of the transition temperature) could be expected by the statistic

replacement of Sr by Ba corresponding to 25% of the competing cations along the c-axis [$(Sr_{0.25}La_{0.75})$-O bond by $(Ba_{0.25}-La_{0.75})$-O one][5]. From the observation of a decrease of the transition temperature (300 to 220 K), however, it should be noted that the lattice expansion ($r_{Sr(II)} = 1.31$ Å, $r_{Ba(II)} = 1.47$ Å)[15] is likely predominant on the competing bond effect on the local crystal-field energy Dq.

The ΔS^o value does not greately change within experimental errors, the entropy change ΔS taking into account of the spin multiplicity difference $\Delta[R\ln(2S+1)]$ and the multiplicities of the vibrational modes ΔS_{vib}

The more negative Γ value observed for the barium phase compared with that for the strontium one can be also associated with an increase of steric effects leading to a compression on the first cationic environment during the spin-state transition of Co(III), which makes difficult the propagation of such a transition into the lattice.

Concluding Remarks

If we compare the influence of the variation of chemical bonding environment in the perovskite-plane with that along the c-axis (Table 2) on the LS→HS transition for trivalent cobalt ion in an oxygen lattice of K_2NiF_4-type, (A, A')$_2M'_{0.5}Co_{0.5}$-O_4 (A' = alkaline earth, A = lanthanide and M' = Mg, Zn), several remarks can be deduced. Replacing the Mg(II) ($Sr_{0.5}$-$La_{1.5}Mg_{0.5}Co_{0.5}O_4$) by the Zn(II) ($Sr_{0.5}La_{1.5}Zn_{0.5}Co_{0.5}O_4$), we observe a decrease of both the transition temperature (T_i) and the enthalpy change characterizing the LS→HS transition. This behavior is attributed to a diminution of the local crystal-field strength on Co(III) site. Such a variation of the Dq/B value can be induced by two physico-chemical factors: the lattice expansion and the increase of the covalency of the competing bonds in the perovskite-planes. If the molar fraction of HS Co(III) at room temperature is not considered, the difference between the size of Mg(II) and Zn(II) ($r_{Mg(II)} = 0.72$ Å, $r_{Zn(II)} = 0.74$ Å) is not sufficient to explain the large ΔH^o variation (~20%). Such a variation should be associated with the increase of the covalency of competing (M'-O) bond from (Mg-O) to (Zn-O) (Pauling's ionicity values are 0.70 and 0.56, respectively). On the other hand, when the strontium ion in $Sr_{0.5}La_{1.5}Zn_{0.5}Co_{0.5}O_4$ lattice is replaced by the barium one which is in competition with (Co-O) bond along the c-axis, the ΔH^o variation is very large (~40%) and the transition temperature also changes from 300 to 220 K. Considering that the variation of the covalency of competing [(A, La)-O] bond is induced by only 25% replacement of cations (0.5 Sr(II) by 0.5 Ba(II) ion), the strong difference in ΔH^o value is attributed to the lattice expansion effect on the spin-state transition of Co(III) ion.

Such comparative studies suggest that the covalency variation be the predominant factor in the perovskite-layers, on the contrary, the lattice expansion resulting from the increase of constituting ions be more important along the c-axis.

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Structure Determination of D-Asparagine by Modified Pseudospectral Hartree-Fock Gradient Method

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Pseudospectral Hartree-Fock(PSHF) gradient calculations with 6-31G** basis set have been carried out to determine the structure of D-Asparagine molecule ($C_4N_2O_3H_8$) with improved grids and with the BFGS method. The modified PSHF method, despite partial optimization of the gradient code, turned out to be still faster than the conventional *ab initio* method, GAUSSIAN 90 program by more than twice. The optimum geometry of D-Asparagine obtained by the PSHF method is in good agreement with those calculated by the GAUSSIAN 90 program (within 0.0036 Å for bond lengths, 0.8 degrees for bond angles, and 1.6 degrees for torsional angles) except for three torsional angles. Here, rather large discrepancy of these three torsional angles (5-6 degrees) is attributed to the small differences in the optimum bond lengths and angles between the PSHF and GAUSSIAN 90 calculations.

Introduction

As is well known, the Hartree-Fock (HF) Quantum mechanical theory has played an important role in the description of chemical and physical properties with reasonable accuracy. However, the HF calculations require large amounts of computation time as the number of basis functions(N) increases. Typically, the formal CPU time is proportional to N^4, so that it would be impractical to perform HF calculations for large molecules. Recently, Friesner's group has developed the Pseudospectral HF (PSHF) method[1~6] which utilizes both a physical space grid and a basis set in the evaluation of two-electron integrals and energy iterations. The PSHF method scales as N^3 (in practice N^2 by the use of cutoffs on local functions) rather than N^4. An order of magnitude improvements in CPU time on a 20 atom HF test case (glutamine) have been achieved[6] as compared to the GAUSSIAN88 computation. The Pseudospectral approach has been successfully extended[7] to the Generalized Valence Bond (GVB)[8] wave function. Also, analytic first derivatives of the HF en-

ergy has been applied in order to determine the structures of several small molecules[9] where both total energies and equilibrium geometries are in good agreement with those obtained from conventional *ab initio* calculations. Because of significant reduction of CPU time, the PSHF gradient method has a great potential to predict molecular structures for large compounds such as biologically important molecules and transition metal complexes. In this paper, we will report the result of the PSHF gradient computation for a medium-size molecule with an improved grid representation as an intermediate step for structure determinations of large-size molecules.

Theoretical Overview

We briefly describe the analytical PSHF gradient method since the detailed derivation was shown in the previous paper[8]. The two-electron integral part (E_{2e}) of the Hartree-Fock energy can be expressed as