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# Fast Computation of Analytical Second Derivatives with Effective Core Potentials: Application to Si<sub>8</sub>C<sub>12</sub>, Ge<sub>8</sub>C<sub>12</sub>, and Sn<sub>8</sub>C<sub>12</sub>

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## Abstract

An improved method is described for the computation of integrals involving effective core potentials. The improved method provides better scalability to higher angular momenta as well as improved speed. The new method is also applied to the determination of the minimum energy structures of Si<sub>8</sub>C<sub>12</sub>, Ge<sub>8</sub>C<sub>12</sub>, and Sn<sub>8</sub>C<sub>12</sub>, main group analogs of the Ti<sub>8</sub>C<sub>12</sub> compounds (known as metcars). Relative energies, geometries, and vibrational frequencies are reported for several novel structures.

## Keywords

Elemental semiconductors, Germanium

## Disciplines

Chemistry

## Comments

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# Fast computation of analytical second derivatives with effective core potentials: Application to $\text{Si}_8\text{C}_{12}$ , $\text{Ge}_8\text{C}_{12}$ , and $\text{Sn}_8\text{C}_{12}$

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An improved method is described for the computation of integrals involving effective core potentials. The improved method provides better scalability to higher angular momenta as well as improved speed. The new method is also applied to the determination of the minimum energy structures of  $\text{Si}_8\text{C}_{12}$ ,  $\text{Ge}_8\text{C}_{12}$ , and  $\text{Sn}_8\text{C}_{12}$ , main group analogs of the  $\text{Ti}_8\text{C}_{12}$  compounds (known as metcars). Relative energies, geometries, and vibrational frequencies are reported for several novel structures. © 1999 American Institute of Physics. [S0021-9606(99)30243-9]

## I. INTRODUCTION

The use of effective core potentials (ECPs)<sup>1</sup> has grown rapidly in recent years as interest in compounds containing elements from the third and subsequent rows of the periodic table has increased. This increase in use has sparked a renewed interest in improving the efficiency of computations involving ECPs. One of the most significant factors influencing the performance of ECPs is the availability of analytic derivatives. Due to the complicated form of the ECP, it is not easy to directly derive analytic derivatives. However, this difficulty was overcome soon after the introduction of the ECP through the application of translational invariance<sup>2,3</sup> to obtain an analytic formula for the energy first derivative (gradient).<sup>4</sup> Later this derivation was extended to include energy second derivatives (Hessians) by Komornicki *et al.*,<sup>5</sup> and has now been implemented by several groups.<sup>6,7</sup> The result of these derivations are the following formulas for the energy, gradient, and Hessian involving ECPs:

$$\text{Energy } E_{\text{ECP}} = \sum_{\mu} \sum_{\nu} \left\langle \phi_{\mu} \left| \sum_C \hat{u}_C \right| \phi_{\nu} \right\rangle, \quad (1)$$

$$\text{Gradient } E_{\text{ECP}}^a = 2 \sum_{\mu} \sum_{\nu} D_{\mu\nu} \left\langle \phi_{\mu}^{\alpha} \left| \delta_{AI} \sum_C \hat{u}_C - \hat{u}_A \right| \phi_{\nu} \right\rangle, \quad (2)$$

$$\begin{aligned} \text{Hessian } E_{\text{ECP}}^{ab} = & 2 \sum_{\mu} \sum_{\nu} D_{\mu\nu} \left( \left\langle \phi_{\mu}^{\alpha\beta} \left| \sum_C \hat{u}_C \delta_{AI} \delta_{BI} - \hat{u}_B \delta_{AI} \right. \right. \right. \\ & \left. \left. - \hat{u}_A \delta_{BI} + \hat{u}_A \delta_{AB} \right| \phi_{\nu} \right\rangle + \left\langle \phi_{\mu}^{\alpha} \left| \sum_C \hat{u}_C \delta_{AI} \delta_{BJ} \right. \right. \\ & \left. \left. - \hat{u}_B \delta_{AI} - \hat{u}_A \delta_{BJ} + \hat{u}_A \delta_{AB} \right| \phi_{\nu}^{\beta} \right\rangle \right). \quad (3) \end{aligned}$$

$E^a$  refers the derivative of the energy with respect to coordinate  $a$  on center  $A$ ,  $\phi_{\mu}$  and  $\phi_{\nu}$  are basis functions located on centers  $I$  and  $J$ , respectively;  $\phi_{\mu}^{\alpha}$  is the derivative of  $\phi_{\mu}$  with respect to a coordinate of center  $I$ ,  $D_{\mu\nu}$  is an element of the density matrix,  $\hat{u}_C$  is the ECP on center  $C$ . Since the derivatives of Gaussian type functions are simply linear combinations of Gaussian functions with different angular momenta,

these equations all represent the same basic ECP integral. However, a derivative of a Gaussian function raises the maximum angular momentum by one for first derivatives and two for second derivatives. Thus, in order to compute the second derivative of a  $g$ -type basis function, basic integrals must be computed over  $h$ - and  $i$ -type functions. Due to the number of integrals with high angular momenta it is important to compute the ECP integrals efficiently. Since the angular portions of the ECP integrals have simple analytic solutions, the main difficulty in the ECP calculation is the computation of the radial integrals.

## II. RADIAL INTEGRAL EVALUATION

There are currently two methods in use for the computation of the radial integrals. The first is the original implementation by Kahn as described in Ref. 1. The second method was proposed by McMurchie and Davidson<sup>8</sup> and has since been improved by several groups.<sup>9</sup> However, a third method, proposed by Kolar,<sup>10</sup> when combined with the original method of Kahn, provides a very efficient method which easily scales to higher angular momenta. Our modifications to the original method of Kahn involve the solution of the general type 2 radial integrals given by the equation (in the notation of Ref. 8)

$$Q_{\lambda\lambda'}^N(k_A, k_B, \alpha) = \int_0^{\infty} dr r^N e^{-\alpha r^2} M_{\lambda}(k_A r) M_{\lambda'}(k_B r). \quad (4)$$

$M_{\lambda}$  is a modified spherical Bessel function of the first kind,  $N$  is defined to be the sum of the powers on  $X$ ,  $Y$ , and  $Z$  for both Gaussian centers, also referred to as  $\kappa$ , plus the power of  $r$  from the ECP projector,  $n_{kl}$  (which may range from 0 for  $s$ -projectors to 4 for  $g$ -projectors). Thus  $N = \kappa + n_{kl}$ . Due to symmetry, the matching angular integrals vanish unless  $\kappa + \lambda + \lambda'$  is even and  $|\lambda - \lambda'| \leq \kappa$ . Also, a recursion relationship for the radial integrals may be derived directly from a standard relationship of the modified spherical Bessel functions:<sup>11</sup>

$$Q_{\lambda,\lambda'}^n = Q_{\lambda-2,\lambda'}^n - \frac{2\lambda-1}{k_A} Q_{\lambda-1,\lambda'}^{n-1}. \quad (5)$$

Using these relationships the number of radial integrals that must be explicitly calculated may be greatly reduced. In fact, the majority of the integrals involve  $\kappa=0$ , and  $\lambda=\lambda'$ . Thus consider:

$$Q_{\lambda\lambda}^{n_{kl}}(k_A, k_B, \alpha) = \int_0^\infty dr r^{n_{kl}} e^{-\alpha r^2} M_\lambda(k_A r) M_\lambda(k_B r). \quad (6)$$

The solutions to this integral are given below using the definitions presented in the Appendix to this paper (for a full derivation please refer to the supplementary material for this paper).<sup>12</sup> Since  $n_{kl} \geq 0$  we need integrals for  $n=(n_{kl}-2) \geq -2$ . For  $n \geq 0$  the following relationships can be derived:

$$B_{0,i} = \sqrt{\frac{\pi}{c}}, \quad (7a)$$

$$C_{0,i} = \sqrt{\frac{\pi}{c}} \operatorname{erf}(a_i \sqrt{c}), \quad (7b)$$

$$B_{1,i} = \frac{1}{c} e^{-ca_i^2} + a_i \sqrt{\frac{\pi}{c}} \operatorname{erf}(a_i \sqrt{c}), \quad (7c)$$

$$C_{1,i} = a_i \sqrt{\frac{\pi}{c}}; \quad (7d)$$

$$B_{n,i} = \frac{n-1}{2c} B_{n-2,i} + a_i C_{n-1,i}, \quad (8a)$$

$$C_{n,i} = \frac{n-1}{2c} C_{n-2,i} + a_i B_{n-1,i}. \quad (8b)$$

For  $n < 0$ :

$$B_{-1,i} = 2\sqrt{\pi} h(a_i \sqrt{c}), \quad (9a)$$

$$C_{-1,i} = 2\sqrt{\pi} d(a_i \sqrt{c}), \quad (9b)$$

$$C_{-2,i} = 4ca_i e^{-ca_i^2} + 2ca_i B_{-1,i} - 2cC_{0,i}, \quad (9c)$$

$$B_{-2,i} = 2ca_i C_{-1,i} - 2cB_{0,i}; \quad (9d)$$

$$B_{-n,i} = (1 + (-1)^{n-1}) \frac{(2ca_i)^{n-1}}{(n-1)(n-1)!} e^{-ca_i^2} - \frac{2c}{n-1} B_{-(n-2),i} + \frac{2ca_i}{n-1} C_{-(n-1),i}, \quad (10a)$$

$$C_{-n,i} = (1 - (-1)^{n-1}) \frac{(2ca_i)^{n-1}}{(n-1)(n-1)!} e^{-ca_i^2} - \frac{2c}{n-1} C_{-(n-2),i} + \frac{2ca_i}{n-1} B_{-(n-1),i}. \quad (10b)$$

Thus all of the integrals for  $n < 0$  are easily related to  $n = -1$  and  $n = 0$  integrals similarly to the relationship between  $n \geq 2$  integrals and  $n = 0$  and  $n = 1$  results. So all possible integrals can be solved in terms of relatively few basic integrals.

This method for the computation of the type 2 radial ECP integrals has been implemented into the GAMESS<sup>13</sup> program. This improvement along with other code modifications has resulted in a significant speedup for the ECP portion of

TABLE I. ECP timings (in CPU seconds on an IBM RS/6000 m370), other one and two electron integral timings included for comparison purposes.

Step	Old code	New code	New code on 2 nodes
Energy 1e-ints.	6.0	6.0	4.0
Energy ECP ints.	218.0	39.0	21.9
Gradient 1e-ints.	45.6	45.6	22.3
Gradient ECP ints.	1178.8	196.0	90.2
Gradient 2e-ints.	2523.4	2523.0	1253.8

calculations. In addition the ECP integral and derivative code has been parallelized by simply dividing up the integrals based upon shells which results in very good scalability. Table I gives some representative timings for a  $\text{Ge}_8\text{C}_{12}$   $T_d$  geometry which will be discussed in detail later in this article. The timings illustrate the speedup over the original version due to Kahn. Specifically the speedups are about 5.5 for energies and 6.0 for gradients. In general the speedup is greater for higher angular momentum functions, thus gradients and Hessians have a higher speedup than energies. Analytic derivatives of ECPs have also been implemented through  $g$ -functions.

### III. CHARACTERIZATION OF THE MINIMUM ENERGY STRUCTURES OF $\text{Si}_8\text{C}_{12}$ , $\text{Ge}_8\text{C}_{12}$ , and $\text{Sn}_8\text{C}_{12}$

As interest in fullerenes and fullerene derivatives has grown in recent years, interest in the smallest fullerene like carbon cage compound,  $\text{C}_{20}$ , has also grown. Several recent studies have examined the minimum energy geometry of  $\text{C}_{20}$ .<sup>14,15</sup> Since many of the interesting properties of fullerenes come from the addition or substitution of metal atoms, it was of great interest when a class of stable 20-atom molecular clusters (8 metal atoms and 12 carbon atoms, referred to as metallocarbohedrenes, or metcars) were reported. In particular, Guo and co-workers have reported the formation of  $\text{M}_8\text{C}_{12}$ , where  $\text{M}=\text{Ti}, \text{V}, \text{Zr}, \text{Hf}, \text{Mo}, \text{or } \text{W}$ , through the reaction of laser vaporized titanium with a variety of hydrocarbon gases.<sup>16</sup> This discovery has prompted several theoretical studies attempting to predict the structures and energetics for a variety of transition metal metcars.<sup>17</sup> Most of these studies have considered two types of arrangements for the minimum energy structure. The first is a distorted dodecahedral structure in  $T_h$  symmetry and the second is a capped tetrahedron in  $T_d$  symmetry. Theoretical studies on  $\text{Ti}_8\text{C}_{12}$  have indicated that the  $T_d$  geometry is much more stable.<sup>17</sup>

Considering the similar electronic structure of main group elements such as silicon, germanium, and tin, and transition metals titanium, zirconium, and hafnium ( $s^2p^2$  vs.  $s^2d^2$ ), it is reasonable to expect similar compounds to exist. Two studies have considered  $\text{Si}_8\text{C}_{12}$ ,<sup>18</sup> however, in both of these the only geometry considered was  $T_h$ . Thus this work will examine silicon, germanium, and tin metcars, with emphasis on the minimum energy structure and lowest electronic states for each system.

#### IV. COMPUTATIONAL METHODS

All structures were initially optimized using the restricted Hartree–Fock (RHF) level of theory for closed shell states and the restricted open shell Hartree–Fock (ROHF) level of theory for open shell electronic states. Since many of the low-lying electronic states have many unpaired electrons in nearly degenerate orbitals, it is likely that a multiconfigurational treatment is needed. Thus, all structures were then fully reoptimized using multiconfigurational self-consistent field (MCSCF)<sup>19</sup> wavefunctions. The MCSCF active space used for all systems was an (8,8) active space. This active space distributes eight electrons among eight orbitals with appropriate consideration of spin and symmetry. This choice allows a full description of all open shell orbitals for all spin states through the nonet (eight unpaired electrons) spin state. The specific active spaces used contained eight nonbonding orbitals for the  $T_h$  isomer, six nonbonding plus one E–C bond/antibond pair for the  $D_2$  isomer, and six nonbonding plus two E–C–E three-center bonding orbitals for the  $D_{2h}$  isomer.

To obtain more accurate energetics single point energies were computed using second-order perturbation theory. For the RHF and ROHF wave functions second-order Møller–Plesset perturbation theory (MP2) was used. For the MCSCF wave functions, second-order multiconfigurational quasidegenerate perturbation theory (MCQDPT2)<sup>20</sup> was used. In addition selected geometries were fully reoptimized using closed shell MP2 wave functions to evaluate the dependence of the geometry on the wave function type.

The basis set used was the SBKJC ECP basis set<sup>21</sup> on Si, Ge, Sn, and a 6-31G(*d*) basis set on C.<sup>22</sup> One set of *d*-type polarization functions was added to each heavy atom.<sup>23</sup> All structures were optimized using analytic gradients and then confirmed by computing the matrix of energy second derivatives, or Hessian, to obtain the harmonic normal modes and corresponding frequencies (each minimum has zero imaginary modes). The calculated frequencies were also used to obtain the harmonic zero-point energies used to convert energy differences to 0 K enthalpy differences.

The GAMESS<sup>13</sup> program was used for all calculations.

#### V. RESULTS

In total, four distinct geometries were considered. In addition to the expected  $T_h$  and  $T_d$  geometries, two other structures were also located, one with  $D_2$  symmetry and one with  $D_{2h}$  symmetry. In each case, the geometry was determined only for the lowest energy spin state for that symmetry. All four geometries are illustrated in Fig. 1 with numbers indicating the symmetry unique atoms. The unique bond lengths are listed in Table II for each molecule at the RHF/ROHF, RMP2, and MCSCF levels of theory. Metal–metal interatomic distances are given for reference even though there are no metal–metal distances short enough to be considered a bond. Table III lists the relative energies of each species at the RHF/ROHF and MCSCF levels, respectively, including the RHF/ROHF zero-point energy (ZPE) correction. The corresponding spin multiplicities are also listed. The absolute

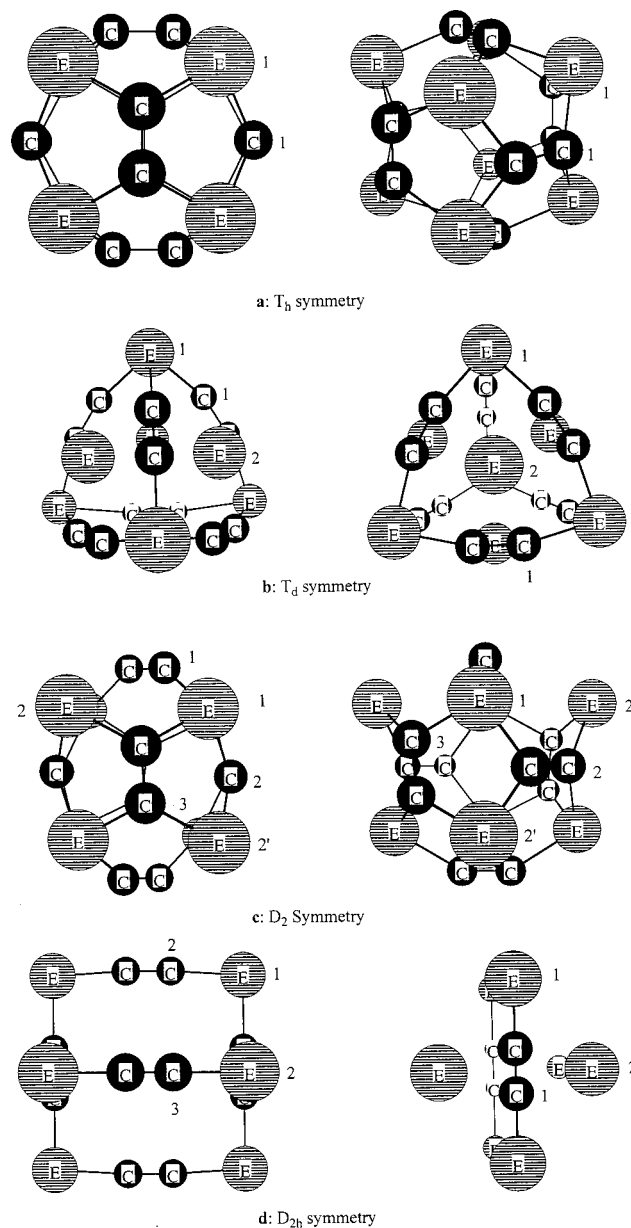


FIG. 1. Structures for  $E_8C_{12}$  (where E=Si, Ge, and Sn).

energies and zero-point energy corrections as well as the complete set of Cartesian coordinates are also included as supplementary material.<sup>12</sup>

From Table III we conclude that although there are some significant differences in the relative energies between RHF/ROHF and MCSCF levels of theory, the qualitative energy order is the same. The same is also true of the geometries listed in Table II, which show only minor differences between the RHF/ROHF bond lengths and those optimized using MCSCF wavefunctions. For the  $T_h$  and  $D_2$  isomers which were first optimized using high-spin ROHF wavefunctions, the MCSCF wavefunction predicts that the lowest energy state is a low-spin open shell configuration with the same number of unpaired electrons as the high-spin state. For comparison with the ROHF result, the high-spin quintet state was also optimized using an MCSCF wave function and is listed in Table III. The nonet state for the  $T_h$  geometry

TABLE II. Optimized bond lengths for Hartree–Fock (HF), RMP2, and MCSCF wavefunctions.

Bond	Si <sub>8</sub> C <sub>12</sub>			Ge <sub>8</sub> C <sub>12</sub>			Sn <sub>8</sub> C <sub>12</sub>		
	HF	MCSCF	MP2	HF	MCSCF	MP2	HF	MCSCF	MP2
<i>T<sub>h</sub></i> geometry									
E–E	3.085	3.088		3.193	3.196		3.698	3.645	3.681
E–C	1.911	1.913		1.986	1.986		2.334	2.302	2.304
C–C	1.351	1.350		1.339	1.338		1.273	1.283	1.323
<i>T<sub>d</sub></i> geometry									
E <sub>1</sub> –E <sub>2</sub>	3.345		3.293	3.503		3.451	3.780		3.727
E <sub>1</sub> –C	1.967		1.944	2.075		2.054	2.269		2.253
E <sub>2</sub> –C	2.402		2.328	2.514		2.436	2.695		2.617
C–C	1.256		1.305	1.253		1.304	1.252		1.302
<i>D<sub>2</sub></i> geometry									
E <sub>1</sub> –E <sub>2</sub>	3.589	3.606		3.676	3.717		3.930	3.926	
E <sub>1</sub> –E' <sub>2</sub>	3.052	3.052		3.186	3.196		3.670	3.700	
E <sub>1</sub> –C <sub>1</sub>	1.877	1.879		1.963	1.976		2.291	2.280	
E <sub>1</sub> –C <sub>2</sub>	1.931	1.940		2.015	2.047		2.359	2.372	
E <sub>1</sub> –C <sub>3</sub>	1.892	1.879		1.969	1.975		2.304	2.294	
E <sub>2</sub> –C <sub>1</sub>	2.935	2.945		2.942	2.929		2.786	2.775	
E <sub>2</sub> –C <sub>2</sub>	1.954	1.951		2.044	2.031		2.272	2.281	
E <sub>2</sub> –C <sub>3</sub>	1.945	1.945		2.040	2.055		2.278	2.274	
C <sub>1</sub> –C <sub>1</sub>	1.215	1.214		1.217	1.218		1.231	1.231	
C <sub>2</sub> –C <sub>2</sub>	1.343	1.340		1.329	1.324		1.276	1.272	
C <sub>3</sub> –C <sub>3</sub>	1.352	1.353		1.337	1.322		1.279	1.277	
<i>D<sub>2h</sub></i> geometry									
E <sub>1</sub> –E <sub>2</sub>	3.217	3.217	3.227	3.372	3.394	3.380	3.661	3.691	3.669
E <sub>1</sub> –C <sub>1</sub>	1.866	1.866	1.868	1.956	1.962	1.969	2.165	2.175	2.174
E <sub>1</sub> –C <sub>2</sub>	1.877	1.877	1.862	1.954	1.954	1.948	2.134	2.134	2.136
E <sub>2</sub> –C <sub>1</sub>	2.116	2.116	2.119	2.250	2.280	2.239	2.449	2.487	2.433
E <sub>2</sub> –C <sub>3</sub>	1.865	1.865	1.845	1.942	1.942	1.932	2.128	2.128	2.125
C <sub>1</sub> –C <sub>1</sub>	1.283	1.283	1.307	1.272	1.261	1.301	1.264	1.253	1.296
C <sub>2</sub> –C <sub>2</sub>	1.208	1.208	1.255	1.208	1.208	1.255	1.211	1.211	1.255
C <sub>3</sub> –C <sub>3</sub>	1.206	1.207	1.252	1.207	1.207	1.254	1.211	1.211	1.255

using an (8,8) MCSCF wave function is identical to the ROHF reference and is therefore not repeated in the MCSCF part of the supplementary material table.

In addition to the expected *T<sub>h</sub>* and *T<sub>d</sub>* structures, Figs. 1(a) and 1(b), a *D<sub>2</sub>* structure, Fig. 1(c), similar to the *T<sub>h</sub>* structure with two of the C<sub>2</sub> units twisted to a nearly linear arrangement between two E atoms, and a *D<sub>2h</sub>* structure, Fig. 1(d), with all C<sub>2</sub> units arranged linearly between pairs of E atoms, were also found. Perhaps surprisingly, the *D<sub>2h</sub>* structure is the preferred geometry at the MCSCF level of theory

TABLE III. SCF and MCSCF relative energies (kcal/mol).

Geometry	Si <sub>8</sub> C <sub>12</sub>		Ge <sub>8</sub> C <sub>12</sub>		Sn <sub>8</sub> C <sub>12</sub>	
	Energy	State	Energy	State	Energy	State
RHF (singlets); ROHF (triplets)						
a <i>T<sub>h</sub></i>	0.0	<sup>9</sup> A <sub>g</sub>	75.5	<sup>9</sup> A <sub>g</sub>	161.9	<sup>1</sup> A <sub>g</sub>
b <i>T<sub>d</sub></i> <sup>a</sup>	259.8	<sup>1</sup> A <sub>1</sub>	172.7	<sup>1</sup> A <sub>1</sub>	123.1	<sup>1</sup> A <sub>1</sub>
c <i>D<sub>2</sub></i>	49.4	<sup>5</sup> A	57.7	<sup>5</sup> A	35.9	<sup>5</sup> A
d <i>D<sub>2h</sub></i>	47.1	<sup>1</sup> A <sub>g</sub>	0.0	<sup>1</sup> A <sub>g</sub>	0.0	<sup>1</sup> A <sub>g</sub>
MCSCF						
a <i>T<sub>h</sub></i>	0.0	<sup>1</sup> A <sub>g</sub>	88.5	<sup>1</sup> A <sub>g</sub>	165.0	<sup>1</sup> A <sub>g</sub>
a <i>T<sub>h</sub></i>	4.9	<sup>9</sup> A <sub>g</sub>	95.2	<sup>9</sup> A <sub>g</sub>		
b <i>T<sub>d</sub></i> <sup>a</sup>						
c <i>D<sub>2</sub></i>	39.6	<sup>1</sup> A	59.9	<sup>1</sup> A	51.6	<sup>1</sup> A
c <i>D<sub>2</sub></i>	50.1	<sup>5</sup> A	74.7	<sup>5</sup> A	54.7	<sup>5</sup> B <sub>2</sub>
d <i>D<sub>2h</sub></i>	46.5	<sup>1</sup> A <sub>g</sub>	0.0	<sup>1</sup> A <sub>g</sub>	0.0	<sup>1</sup> A <sub>g</sub>

<sup>a</sup>Saddle point at the RHF level of theory.

for the germanium and tin systems, while the *T<sub>h</sub>* geometry is preferred by the silicon system. The *D<sub>2</sub>* geometry is 35–60 kcal/mol higher than the minimum energy geometry for each system. The *T<sub>d</sub>* geometry is found to be quite high in energy for all three systems, and Hessians reveal that it is a high order saddle point with several normal modes which break the *T<sub>d</sub>* symmetry. As the metal is changed from Si to Ge and Sn, the *T<sub>h</sub>* geometry becomes much less favorable, while the *D<sub>2h</sub>* geometry becomes more favorable.

Table II illustrates that as the metal is changed from Si to Ge and Sn the metal–metal (E–E) and metal–carbon (E–C) distances increase, as might be expected from the increasing atomic radius of the metal atom. Perhaps less expected is the observation that as the radius of the metal atom increases the C–C bond distance stays the same or decreases. There is also a dramatic difference in the C–C bond distance among the four isomers. In the *T<sub>h</sub>* isomer the C–C bond distance of approximately 1.34 Å is characteristic of a C–C double bond. However, the C–C distance of 1.21 Å in the *D<sub>2h</sub>* isomer indicates a C–C triple bond. Thus, there is a significant difference in the bond character between the different isomers. These compare to a C–C bond distance between 1.4–1.5 Å for C<sub>20</sub> (Ref. 14) and a value of 1.4 Å for the Ti<sub>8</sub>C<sub>12</sub> metacars.<sup>18</sup>

The *D<sub>2</sub>* and *D<sub>2h</sub>* structures have fewer E–C bonds than the *T<sub>h</sub>* structure. In the *T<sub>h</sub>* structure every metal atom is directly bonded to three carbon atoms. In the *D<sub>2</sub>* structure

TABLE IV. MP2 and MCQDPT2 relative energies (kcal/mol).

Geometry	Si <sub>8</sub> C <sub>12</sub>		Ge <sub>8</sub> C <sub>12</sub>		Sn <sub>8</sub> C <sub>12</sub>	
	Energy	State	Energy	State	Energy	State
MP2//SCF						
a $T_h$	0.0	<sup>9</sup> A <sub>g</sub>	72.8	<sup>9</sup> A <sub>g</sub>	4.9	<sup>1</sup> A <sub>g</sub>
b $T_d^a$	79.5	<sup>1</sup> A <sub>1</sub>	34.1	<sup>1</sup> A <sub>1</sub>	4.1	<sup>1</sup> A <sub>1</sub>
c $D_2$	17.0	<sup>5</sup> A	62.1	<sup>5</sup> A	6.8	<sup>5</sup> A
d $D_{2h}$	19.7	<sup>1</sup> A <sub>g</sub>	0.0	<sup>1</sup> A <sub>g</sub>	0.0	<sup>1</sup> A <sub>g</sub>
MCQDPT2//MCSCF						
a $T_h$	0.0	<sup>1</sup> A <sub>g</sub>	28.4	<sup>1</sup> A <sub>g</sub>	-9.2	<sup>1</sup> A <sub>g</sub>
c $D_2$	45.9	<sup>1</sup> A	9.8	<sup>1</sup> A	-26.5	<sup>1</sup> A
c $D_2$	72.3	<sup>5</sup> A	51.6	<sup>5</sup> A	-13.0	<sup>5</sup> B <sub>2</sub>
d $D_{2h}$	68.6	<sup>1</sup> A <sub>g</sub>	0.0	<sup>1</sup> A <sub>g</sub>	0.0	<sup>1</sup> A <sub>g</sub>
MP2//RMP2						
a $T_h$					3.6	<sup>1</sup> A <sub>g</sub>
b $T_d^a$	62.6 <sup>(b)</sup>	<sup>1</sup> A <sub>1</sub>	30.5	<sup>1</sup> A <sub>1</sub>	0.8	<sup>1</sup> A <sub>1</sub>
d $D_{2h}$	7.3 <sup>(b)</sup>	<sup>1</sup> A <sub>g</sub>	0.0	<sup>1</sup> A <sub>g</sub>	0.0	<sup>1</sup> A <sub>g</sub>

<sup>a</sup>Saddle point at the RHF and MP2 levels of theory.

<sup>b</sup>Relative to the  $T_h$  MP2 single point energy.

the affect of twisting two of the C<sub>2</sub> units is to reduce the E–C bond count on four of the metal atoms. This reduction results in increased bonding for the affected C<sub>2</sub> units, as well as a small reduction in the bond length of the remaining E–C bonds. This effect is even greater in the  $D_{2h}$  structure, in which four of the metal atoms are directly bonded to two carbon atoms. The remaining four metal atoms are directly bonded to only one carbon atom and bridge a C<sub>2</sub> unit. Thus, the reduction in the number of direct metal–carbon bonds in the  $D_{2h}$  structure results in an increased bond order for the C–C bonds as well as a small increase in the bond order for the remaining metal–carbon bonds.

All of these results can probably best be described as size effects of the metal atom. As the size of the metal atom increases the length of the metal carbon bonds must also increase. In these cage structures, especially the  $T_h$  structure, this pushes the metal atoms farther from the cage center and decreases the angle between metal–carbon bonds, thus increasing the cage strain. In addition, the metal–carbon bond strength for Ge and Sn is lower than for Si due to the less effective overlap of the 4*p* and 5*p* orbital with the 2*p* of carbon. Thus, the Ge and Sn systems prefer arrangements where the carbon–carbon bond order is high at the expense of the number of metal–carbon bonds such as the  $D_{2h}$  structure.

Table IV lists the RMP2/ROMP2 and MCQDPT2 relative energies, without ZPE correction. The addition of dynamic correlation provided by perturbation theory dramatically shifts the relative energies. The primary affect is a considerable reduction in the spread of energies among the isomers. Nonetheless, the global minimum for each species is unchanged, except in the case of Sn<sub>8</sub>C<sub>12</sub>. In the latter case, the MCQDPT2 global minimum is predicted to be  $D_2$  <sup>1</sup>A. To assess the effect of perturbation theory on the geometries, the isomers for which RMP2 provides an adequate description were fully reoptimized at the MP2 level of theory. The resulting energies are listed in Table IV and the optimized bond lengths are included in Table II. Since MCQDPT2 op-

timizations are not currently possible, further optimizations were not performed.

The MP2 optimizations do not change the relative energies dramatically, even though there is a noticeable lengthening of the C–C bonds (0.3–0.5 Å). Thus, the single point energies probably provide a good estimate of the relative ordering of the energies of each isomer. In addition, MP2 Hessians predict that the  $T_d$  isomers are high order saddle points in agreement with the RHF results. Therefore, we conclude that SCF and MCSCF wave functions seem to be adequate to get the correct basic energy order and geometries, while perturbation theory is necessary to get the correct magnitudes of the energy differences.

The vibrational frequencies with significant infrared intensities are listed in Table V. A simple description is also listed for each frequency, but since the majority of the frequencies involve the entire cluster it is necessary to view animations of each vibration to fully understand the motion of the molecule (animations are provided in the supplementary material).<sup>12</sup> Except for two systems where a C<sub>2</sub> stretch is infrared active, all of the listed frequencies involve at least four atoms, such as E–C–C–E stretches, and many involve the entire cage. Most of the low frequency vibrations involve the motion of the C<sub>2</sub> as a unit, either in a twisting motion about the center of the C–C bond or as a concerted motion in one direction.

## VI. CONCLUSIONS

In this article we have presented an improved method for the computation of integrals involving effective core potentials. This improved method has been implemented into the GAMESS program and has been shown to significantly reduce the computational cost of ECP integrals. The improved program has been applied to the determination of the minimum energy structures of silicon, germanium, and tin analogs of the Ti<sub>8</sub>C<sub>12</sub> metcars. In addition to the two expected structures, two novel previously unreported arrangements have also been predicted.

The predicted geometries and relative energies for each isomer show that three isomers, the  $T_h$ ,  $D_2$ , and  $D_{2h}$  structures, correspond to energy minima, while the fourth isomer, the  $T_d$  structure, is a high-order saddle point. The  $T_h$  structure is predicted to be the global minimum for Si<sub>8</sub>C<sub>12</sub> at all levels of theory. In contrast the  $D_{2h}$  structure is predicted to be the global minima for Ge<sub>8</sub>C<sub>12</sub>, and  $D_2$  is predicted to be the Sn<sub>8</sub>C<sub>12</sub> global minimum at the MCQDPT2//MCSCF level of theory, which predicts the  $D_2$  structure to be the global minima.

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TABLE V. Vibrational frequencies with an infrared intensity greater than 0.1 Debye<sup>2</sup>/(amu Å<sup>2</sup>).

Geometry	Si <sub>8</sub> C <sub>12</sub>		Ge <sub>8</sub> C <sub>12</sub>		Sn <sub>8</sub> C <sub>12</sub>		Type <sup>a</sup>
	Frequency	Intensity	Frequency	Intensity	Frequency	Intensity	
a <i>T<sub>h</sub></i>	499	1.4	484	4.3	403	3.3	cs
	499	1.4	484	4.3	403	3.3	cs
	499	1.4	484	4.3	403	3.3	cs
	568	4.1	649	0.2	567	0.4	cr
	568	4.1	649	0.2	567	0.4	cr
	568	4.1	649	0.2	567	0.4	cr
	808	3.2	690	0.8			ca
	808	3.2	690	0.8			ca
	808	3.2	690	0.8			ca
					1587	0.2	c2
					1587	0.2	c2
					2587	0.2	c2
	c <i>D<sub>2</sub></i>	160	0.5	135	0.2	103	0.1
166		0.5	144	0.2			cb
279		0.5	205	0.8	138	0.3	cb
282		0.1	216	0.5	187	0.3	cs
317		0.2	216	0.1	165	0.8	cb
330		0.2			247	0.8	cs
356		0.2			277	1.0	cr
306		0.2			278	0.6	cs
374		0.2	373	0.6	280	0.3	cr
424		0.6	391	0.4	299	0.7	cs
475		2.0	406	2.1	332	0.7	cs
497		1.3	408	0.2			cr
528		1.5	428	0.8	337	1.0	cr
553		5.0	453	2.1	358	1.4	cs
			457	0.2			cs
			458	1.1	391	4.6	cs
626		0.2	546	0.4	416	0.6	cr
641		1.2	558	2.4	450	0.2	cr
678		2.3	576	4.0	452	2.0	cs
687		0.6	594	1.1			cs
			604	0.9			cr
			619	0.7			cr
699		0.2					cs
715		4.0	686	1.3	454	1.3	cs
735		0.7					ca
739		2.5	689	1.9	471	0.6	ca
805		0.5			479	7.9	cs
822	5.8	737	0.8	492	0.6	cs	
2295	0.1	1620	0.2			c2	
d <i>D<sub>2h</sub></i>	262	0.1	233	0.4	188	0.8	eb
	279	0.5	239	0.4	198	0.6	eb
	307	0.7	239	0.2	195	0.3	er
			246	0.2			es
			269	0.2			es
	440	0.6	378	0.3	304	0.3	cr
	538	4.5	461	3.3	368	3.4	cr
	571	0.6	484	12.7	423	8.5	es
	606	21.3	514	0.7	441	0.6	cr
	723	0.7	600	0.2			es
	746	24.2	611	19.6	526	14.7	es
	780	32.2	654	29.0	584	30.7	es

<sup>a</sup>Codes: cs=symmetric cage stretch, ca=asymmetric cage stretch, cb=cage bend, cr=C<sub>2</sub> rocking motion, c2=C-C bond stretch, eb=E-C-C-E bend, er=E-C-C-E rock, es=E-C-C-E stretch.

## APPENDIX

Included below are definitions of each term presented in the solutions to the ECP radial integral equation. Since the majority of the integrals involve  $k=0$ , and  $l=1'$ , the integral in Eq. (6) reduces to

$$Q_{\lambda\lambda}^{nkl}(k_A, k_B, \alpha) = \int_0^\infty dr r^{nkl} e^{-\alpha r^2} M_\lambda(k_A r) M_\lambda(k_B r). \quad (\text{A1})$$

$M_\lambda$  are modified spherical Bessel functions given by

$$M_k(x) = (-1)^{k+1} \sum_{i=1}^k \frac{\alpha_{ik}}{x^i} \cosh(x) + (-1)^k \sum_{i=1}^k \frac{\beta_{ik}}{x^i} \sinh(x), \quad (\text{A2})$$

where  $\alpha$  and  $\beta$  are integer coefficients defined in Ref. 11. General  $Q$  integrals then reduce to combinations of the following:

$$\rho_n = \int_0^\infty e^{-cr^2} \sinh(k_A r) \sinh(k_B r) r^n dr, \quad (\text{A3a})$$

$$\sigma_n = \int_0^\infty e^{-cr^2} \sinh(k_A r) \cosh(k_B r) r^n dr, \quad (\text{A3b})$$

$$\bar{\sigma}_n = \int_0^\infty e^{-cr^2} \cosh(k_A r) \sinh(k_B r) r^n dr, \quad (\text{A3c})$$

$$\tau_n = \int_0^\infty e^{-cr^2} \cosh(k_A r) \cosh(k_B r) r^n dr. \quad (\text{A3d})$$

It is also convenient to make the following definitions:

$$A_n(c, a_i) = \int_{-a_i}^\infty e^{-cx^2} (x + a_i)^n dx, \quad (\text{A4a})$$

$$a_1 = \frac{k_A + k_B}{2c}, \quad (\text{A4b})$$

$$a_2 = \frac{|k_A - k_B|}{2c}, \quad (\text{A4c})$$

$$\Gamma_i = \frac{1}{4} e^{ca_i^2}, \quad (\text{A4d})$$

$$B_{n,i} = A_n(c, a_i) + A_n(c, -a_i), \quad (\text{A5a})$$

$$C_{n,i} = A_n(c, a_i) - A_n(c, -a_i). \quad (\text{A5b})$$

The above integrals then become:

$$\rho_n = \Gamma_1 B_{n,1} - \Gamma_2 B_{n,2}, \quad (\text{A6a})$$

$$\tau_n = \Gamma_1 B_{n,1} + \Gamma_2 B_{n,2}, \quad (\text{A6b})$$

$$\sigma_n = \Gamma_1 C_{n,1} + \text{sign}(k_A - k_B) \Gamma_2 C_{n,2}, \quad (\text{A6c})$$

$$\bar{\sigma}_n = \Gamma_1 C_{n,1} - \text{sign}(k_A - k_B) \Gamma_2 C_{n,2}. \quad (\text{A6d})$$

The solution of these integrals will involve three special functions: the error function:

$$\text{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt, \quad (\text{A7})$$

the Dawson function:

$$d(x) = e^{-x^2} \int_0^x e^{t^2} dt, \quad (\text{A8})$$

and the hybrid Dawson error function:

$$h(x) = e^{-x^2} \int_0^x e^{t^2} \text{erf}(t) dt. \quad (\text{A9})$$

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