



Energetics of carbon clusters C_{20} from all-electron quantum Monte Carlo calculations

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Abstract

The energetics of the ring, bowl, and cage isomers of C_{20} were determined in all-electron fixed-node quantum Monte Carlo calculations. In good agreement with results from valence-only quantum Monte Carlo calculations and from Møller–Plesset calculations with large basis sets, the calculations predict the lowest-energy isomer to be the bowl isomer. The energies of the ring and cage, relative to the bowl, are 1.1 ± 0.5 and 2.1 ± 0.5 eV, respectively. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

It is fairly well established that among the numerous stable isomers of the carbon cluster C_{20} – which include chains, rings, bowls, plates, cages, and combinations of these – the lowest in energy are the ring, bowl, and cage illustrated in Fig. 1 [1–13].

For these three, however, the available theoretical methods give a variety of differing predictions for the relative energies. In general, as shown in Table 1, Hartree–Fock (HF) calculations favor the ring; Møller–Plesset (MP2) calculations with small basis

sets favor the cage and with large basis sets favor the bowl; coupled-cluster (CCSD and CCSD(T)) favor the bowl and cage; density functional (LDA, BLYP, and B-PW91) calculations favor the cage, ring, and bowl; and valence-only (pseudopotential) quantum Monte Carlo (pspQMC) calculations favor the bowl. The relative energies predicted by the several methods vary in the range of several eV and such differences can shift an equilibrium constant by a large factor, $\exp(\Delta E/kT) = 10^{16}$ for 2 eV at 600 K.

Some information is available from experimental measurements. For the ions C_{20}^+ and C_{20}^- there is evidence for linear-chain structures, mono- and bicyclic rings, and tadpole (ring and chain) isomers [14–19]. Recent Raman spectra of C_{20} clusters in nitrogen matrices are consistent with the linear-chain isomer but inconsistent with the bowl and cage isomers [20].

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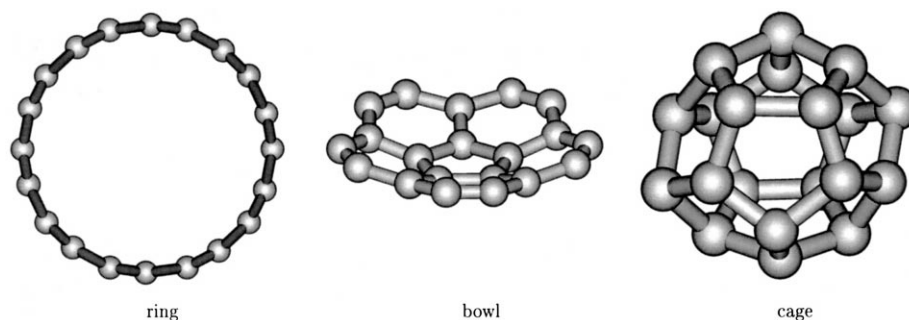


Fig. 1. Isomers of C₂₀.

We report here all-electron fixed-node quantum Monte Carlo calculations for the ring, bowl, and cage isomers.

2. Computational details

Our all-electron quantum Monte Carlo (QMC) calculations for C₂₀ were carried out in exactly the same manner as those we reported earlier for C₈ and C₁₀ clusters [21]. The trial wavefunctions for importance sampling and fixing the nodes were derived in the same way from Gaussian [22] calculations with 10-31G* basis sets and replacement of 1s Gaussian orbitals with Slater-type orbitals. The Jastrow functions were optimized by minimizing the variance in local energies in variational QMC calculations. The standard deviation in local energies was about 4.7 Hartrees for each of the structures. The calculations were executed on parallel IBM SP2 computers located at the Pennsylvania State University.

The nuclear geometries used are those determined by Raghavachari [9] in complete geometric optimizations at the SCF level with a polarized double-zeta 6-31G* basis set. Identical geometries have been used in LDA, BLYP/HF, and BLYP calculations by the same authors, in valence (pseudopotential) pspQMC calculations by Grossman et al. [4], and in pseudospectral MP2 calculations by Murphy and Friesner [7].

The effect of different optimizations of the geometries on the relative energies is relatively small as indicated in comparisons by Taylor et al. [12] for SCF- and LDA-optimized structures with SCF, MP2, CCSD, LDA, and B3LYP calculations. Nevertheless,

we caution that our calculations reported here do not include any additional geometry optimizations.

In our calculations, we used time-step sizes of 0.002–0.007 a.u. at intervals of 0.001 a.u. The total energies for each isomer were obtained by extrapolation to zero time-step size. The uncertainties associated with the extrapolations are included in the indicated statistical errors.

The fixed-node QMC calculations are variational with respect to the locations of the nodal surfaces. For the calculations reported here the nodes are those given by the single-determinant SCF importance-sampling trial functions. The Jastrow function lowers the expectation value of the energy to a value (typically well below the HF limit) which may be determined in variational QMC calculations (VQMC) using Metropolis sampling. The VQMC energies so determined are listed in Table 2. The fixed-node calculations give the energies corresponding to exact solutions of the Schrödinger equation for the nodal surfaces (i.e., boundary conditions) specified. These energies are expected to be higher than the true energies by 10–20 kcal/mol per carbon atom. In comparing the energies of similar systems most of the fixed-node error is expected to cancel, so that energy differences are expected to be more accurate than total energies [12,13].

3. Results and discussion

Results, in terms of total energies, are listed in Table 2. Typical results for other types of calculations giving total energies are shown for comparison. The all-electron QMC values lie about 4 Hartrees

Table 1
Isomers of C₂₀. Relative energies in eV

Method		Ring	Bowl	Cage	Lowest
Authors	Type and basis				
Semi-empirical					
sa	AM1	<u>0.0</u>	14.7	12.5	ring
mf	PS-J1(3d2f)	1.2	<u>0.0</u>	2.2	bowl
HF					
pa	HF (11s6p)/[5s4p] + d	0.0	–	4.6	–
mf	HF cc-pVTZ(+ +)	<u>0.0</u>	1.4	4.4	ring
tbwk	HF --	<u>0.0</u>	0.9	3.4	ring
rsospjg	HF 6-31G *	<u>0.0</u>	1.4	4.0	ring
gmr	HF 6-311G *	<u>0.0</u>	1.7	4.5	ring
wdp	HF 6-31G(d)	<u>0.0</u>	1.1	3.6	ring
wdp	HF DH DVZ(p)	<u>0.0</u>	0.5	2.7	ring
MP2					
pa	MP2 (11s6p)/[5s4p] + d	3.2	–	0.0	–
tbwk	MP2 --	3.9	0.8	<u>0.0</u>	cage
wdp	MP2 6-31G(d,p)	2.7	<u>0.0</u>	0.9	bowl
wdp	MP2 DH DVZ(P)	3.5	<u>0.0</u>	0.5	bowl
mf	LMP2 cc-pVTZ(+ + /3d2f)	1.8	<u>0.0</u>	1.4	bowl
mf	GVB-LMP2 cc-pVTZ(-f)	1.0	<u>0.0</u>	2.7	bowl
Density functional					
js	LDA TZ94AUX	2.2	0.8	<u>0.0</u>	cage
badkzbt	LDA CP/psp/pw	2.7	0.8	<u>0.0</u>	cage
gmr	LDA 6-311G *	4.3	1.1	<u>0.0</u>	cage
tbwk	LDA --	3.3	0.8	<u>0.0</u>	cage
btkw	LDA psp + pw	2.4	0.8	<u>0.0</u>	cage
rsospjg	LDA 6-311G	3.8	1.0	<u>0.0</u>	cage
wdp	LDA 6-31G(d,p)	3.9	1.5	<u>0.0</u>	cage
ggg	LDA psp + pw	2.5	0.6	<u>0.0</u>	cage
ggg	PBE psp + pw	<u>0.0</u>	0.2	1.0	cage
js	GC TZ94AUX	<u>0.0</u>	0.7	1.7	ring
rsospjg	BLYP/HF 6-311G	<u>0.0</u>	0.6	3.8	ring
rsospjg	BLYP 6-311G	<u>0.0</u>	1.1	3.4	ring
wdp	BLYP 6-31G(d,p)	<u>0.0</u>	1.5	3.3	ring
gmr	BLYP 6-311G *	<u>0.0</u>	1.1	3.4	ring
mef	B3LYP cc-pVDZ	0.6	<u>0.0</u>	1.4	bowl
gmr	B3LYP 6-311G *	<u>0.0</u>	0.4	2.3	ring
gmr	B-PW91 6-311G *	0.5	<u>0.0</u>	0.8	bowl
gmr	B3-PW91 6-311G *	0.8	<u>0.0</u>	0.7	bowl
Coupled cluster					
tbwk	CCSD(T) cc-pVDZ	2.8	<u>0.0</u>	0.6	bowl
tbwk	CCSD(T) + est.	2.6	0.2	<u>0.0</u>	cage
btkw	CCSD --	1.5	<u>0.0</u>	0.7	bowl
btkw	CCSD(T) cc-pVDZ	1.7	<u>0.0</u>	<u>0.0</u>	bowl/cage
Quantum Monte Carlo					
gmr	pspQMC	1.1	<u>0.0</u>	2.2	bowl
this work	aeQMC	1.1	<u>0.0</u>	2.1	bowl

badkzbt [1]; btkw [2]; ggg [3]; gmr [4]; js [5]; mef [6]; mf [7]; pa [8]; rsospjg [9]; sa [10,11]; tbwk [12]; wdp [13].

Table 2
Calculated total energies for C₂₀ isomers

Authors	Total energy (Hartree)		
	Ring	Bowl	Cage
Wang et al. [13]			
HF DH DVZ(p)	–756.756	–756.738	–756.658
MP2 DH DVZ(p)	–759.168	–759.296	–759.278
BLYP 6-31G(d,p)	–761.600	–761.544	–761.478
Taylor et al. [12]			
CCSD(T)	–759.312	–759.404	759.394
This work			
HF trial w/o Jastrow	–756.689	–756.651	–756.558
HF trial w Jastrow (VQMC)	–759.236	–758.968	–759.058
± statistical error ^a	±0.011	±0.011	±0.011
all-electron FN-QMC	–760.825	–760.865	–760.788
± statistical error ^a	±0.013	±0.013	±0.013
Experiment			
estimate, see text	–761.5	–761.5	–761.5

^a Statistical error in relative energies is different from that shown for total energies.

lower than the HF values, about 1.6 Hartrees lower than the MP2 values, and about 1.5 Hartrees below the CCSD(T) values. The BLYP values are still lower by about 0.7 Hartrees. Except for the indicated statistical error the all-electron QMC values represent variational upper bounds and are higher than the exact values by the fixed-node errors.

The estimated exact values of the total energy, derived as in Ref. [21] from the energy of free carbon atoms together with the estimated binding energies, are also listed in Table 2. From these the fixed-node error is estimated to be 20 kcal/mol and the recovery of correlation energy is estimated to be 85%.

The relative energies obtained for the three isomers are listed at the bottom of Table 1. The bowl has the lowest energy and the energies for the ring and cage, relative to the bowl, are, 1.1 ± 0.5 and 2.1 ± 0.5 eV, respectively.

Our relative energies are in good agreement with those of the earlier valence QMC calculations of Grossman et al. [4] and with those of large-basis-set MP2 calculations, in particular, the pseudospectral MP2 calculations of Murphy and Friesner [7]. The nuclear geometries for these three studies are the same.

Our QMC calculation method was identical to that we used previously for C₈ and C₁₀. Since our calculations for C₈ and C₁₀ were in quantitative agreement with calculations using all available high-level methods, there is good evidence for the reliability of our procedure. Similar comparisons give good evidence for the reliability of the valence QMC calculations and large-basis-set MP2 calculations for C₂₀.

The fixed-node all-electron QMC calculations are in excellent agreement with previous valence QMC simulations. The MP2 calculations with large basis sets and the B-PW91 and B3-PW91 density functional methods also favor the bowl isomer, but the cage isomer energy lies too low relative to bowl and ring. The coupled-cluster calculations correctly identify the ring isomer as having the highest energy, but have difficulty differentiating the bowl from the cage.

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