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Obtaining the right orbitals is the first step to calculating accurate binding energies for Cu^+ ion

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Abstract

We investigate the previously reported poor performance of the G2 method for simple copper systems. We optimized CuH^+, CuO^+, and $CuSi^+$ using the HF, MP2, B3LYP, mPW1PW91, and MPW1K methods with three basis sets. We found multiple solutions to the Hartree–Fock equations, which are the cause for previously reported poor behavior of the G2 method. The orbitals of the lowest-energy unrestricted Hartree–Fock solution do not always generate the lowest-energy correlated wavefunction. Hybrid density functional theory methods are shown to be quite successful for obtaining orbitals and for predicting geometries and atomization energies. © 2002 Published by Elsevier Science B.V.

1. Introduction

The chemistry of copper is important for many systems of biological and industrial significance. For this reason, numerous experimental [1–4] and theoretical [5–11] studies have been carried out on simple copper systems. A recent paper in this journal [9] entitled 'Cu$^+$ Binding Energies. Dramatic Failure of the G2 method vs. Good Performance of the B3LYP Approach' reported the surprising result that GAUSSIAN-2 (G2) theory [12] predicts negative bond energies for Cu$^+$ with H and O, which was interpreted as due to HF 'instabilities'. Even when these instabilities were eliminated, the predicted binding energies were

found to differ from experiment by 14–25 kcal/mol. The authors attributed the large errors to the poor convergence of the Møller–Plesset (MP) perturbation series. This prompted us to re-examine these systems with Hartree–Fock (HF) theory [13], second-order MP (MP2) perturbation theory [14], and modified Perdew–Wang (mPW) hybrid density functional theory (HDFT) [15,16]. We found that the problem raises fascinating issues of multiple roots for the self-consistent field (SCF) orbitals, similar to difficulties noted by Ghanty and Davidson [17] in earlier work. In the present paper, we report a study that sorts out the issues with new HF, MP2, G2, and HDFT calculations.

The best way to obtain orbitals for an electronic structure calculation is to solve a set of SCF equations, for example, the HF equations, for the coefficients of a set of basis functions in which the

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orbitals are expanded. The SCF iterations are not guaranteed to converge to the lowest-energy solution of the HF equations. For example, one can obtain both minima and saddle points in the coefficient space. Even if a minimum is obtained, it is not guaranteed to be the absolute minimum energy in coefficient space for a fixed geometry. The PEF (potential energy function) generated by always taking the lowest-energy solution to the HF equations will have cusps if the lowest-energy solution jumps discontinuously in atomic orbital (AO) coefficient space. This SCF convergence problem can be more serious in metal complexes because there can be several states with similar energies. Although SCF methods like HF are a good way to obtain orbitals, an accurate energy calculation requires the addition of correlation energy. The calculation of the correlation energy is usually based on the HF orbitals. To be certain of finding the lowest-energy correlated wavefunction, it may be necessary to try more than one set of orbitals because the lowest-energy correlated wavefunction does not necessarily come from the lowest-energy HF solution.

Due to the expense of geometry optimization, it is common practice to perform high-level calculations on a structure optimized at a lower level of theory and/or with a smaller basis set. The // method (in which the geometry is optimized at a lower level than is used for the energy calculation) [18] has been shown to be a useful method for predicting thermochemical properties of molecules containing first and second row atoms. These // methods have not been well tested on copper compounds, and, in addition to examining the orbital problem, we will also investigate the error introduced by this method.

Multilevel methods (methods, usually with empirical parameters, that are based on a combination of energies calculated at various levels of theory and/or with various basis sets) have been shown to be cost effective for predicting thermochemical information [12,19–24]. Most multilevel methods include both HF and correlated components. It is interesting to see how a multilevel method like G2 [12], which did not have a copper compound in its training set, performs on these difficult systems. Section 2 summarizes all methods

and basis sets used in the present paper. Section 3 presents results, Section 4 has discussion, and Section 5 has conclusions.

2. Methods

All electronic structure calculations were performed with the GAUSSIAN 98 program [25]. The basis sets used were 6-31G(d) basis [26–28], the 6-31+G(d,p) basis [18], and the MG3 basis [21]. The MG3 basis set is a modified version of the G3Large basis set; after we submitted our first paper using this basis set, a paper by Curtiss et al. [29] appeared in which the identical modification was independently suggested and called G3Large-eMP2. The MG3 basis was extended to include copper by using the 6-311+G(3d2f) basis set [30] for basis functions on copper. All calculations are based on the spin-unrestricted formalism, in which the zero-order HF wavefunction is a single Slater determinant for the wavefunction or reference state, with different orbitals for different spins and no spin projection operators. With this understood, we omit the U prefix in UHF, UMP2, etc.

The single-level methods used were HF, MP2, and HDFT. The three HDFT methods tested were mPW1PW91 [15], B3LYP [31], and MPW1K [16]. The one multilevel method tested was G2 [12].

Experimental values [1,4] of ΔH_0^0 for the reaction

$$CuX^+ \rightarrow Cu^+ + X \qquad (1)$$

are used to compare binding energies. For methods other than G2, the zero point energy (ZPE) that is added to the electronic energy to calculate ΔH_0^0 was calculated harmonically at the mPW1PW91/MG3 level. In G2, ZPE is always calculated by the scaled HF/6-31G(d) [32] method.

3. Results

We found that SCF convergence is sensitive to the initial geometry and to the initial orbital guess. We tried several different kinds of initial guesses for the orbitals in an attempt to find the best

solutions to the HF equations. With both the 6-31G(d) and MG3 basis sets, three solutions were found to the HF equations for CuO^+, two solutions were found for CuH^+, and only one solution was found for $CuSi^+$. For CuO^+, the three solutions can be obtained using three combinations of different initial guesses. The three initial guesses are: (A) the converged spin-restricted Hartree–Fock wavefunction, (B) the extended Hückel wavefunction followed by HOMO–LUMO orbital mixing, and (C) the extended Hückel wavefunction itself. The three solutions, labeled A, B, and C, have qualitative differences for several of the orbitals.

In Fig. 1, the HF/6-31G(d) energies of three different SCF solutions are plotted against the internuclear separation of CuO^+. These are all converged SCF solutions of the HF wavefunction. The three solutions have minima at 1.75, 2.02, and 2.54 Å. It is interesting to note that each solution is the lowest-energy solution at its own minimum. As a result, if we always choose the lowest-energy solution, there are two cusps in the potential curve.
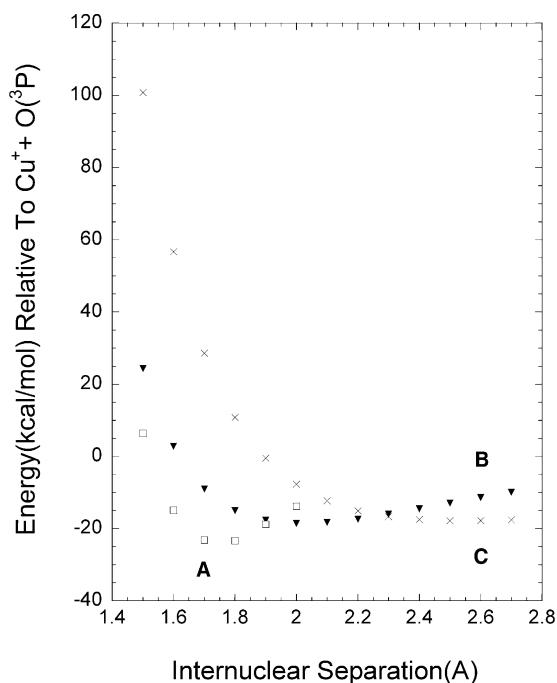
In Fig. 2, we see that the MP2 potential curves using the three reference functions are qualitatively different from their HF counterparts. Solution B has the lowest MP2 energy over the entire range examined. The binding energies and equilibrium geometries for CuO^+ optimized with the three different solutions are listed in Tables 1 and 2.

The three orbital solutions were used as an initial guess for the HDFT methods investigated. The dipole moment for CuO^+ calculated with different levels of theory and basis sets are listed in Table 3 for all three SCF solutions found. The 11 lowest energy α-spin and β-spin orbitals are very similar for all three SCF solutions with every method investigated. The remaining eight α-spin and six β-spin occupied orbitals, as well as the dipole moment, are used to differentiate between the three molecular orbital solutions. The three solutions are simply labeled solutions A, B, and C. Solution A is characterized by a dipole moment of 3.0–6.6 D (where 1 D = 1 debye) and a very consistent set of orbitals with all the methods explored. For description of the orbitals, we let the

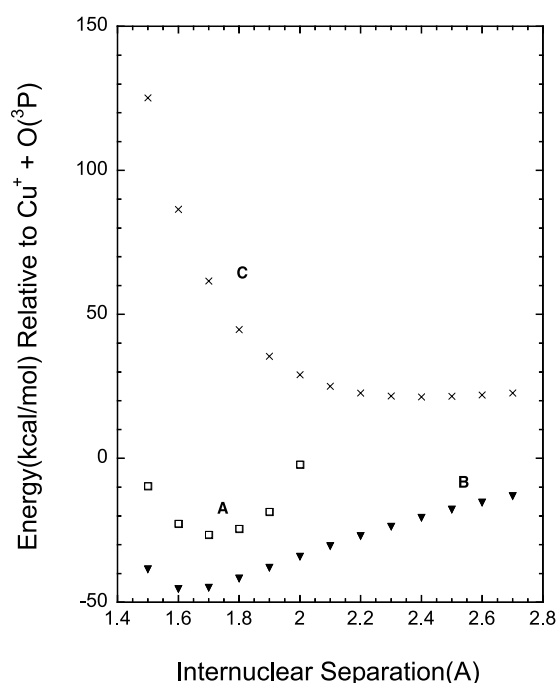

Fig. 1. PEF generated from the three UHF/6-31G(d) solutions for CuO^+: (□) solution A; (▼) solution B; (×) solution C.

Fig. 2. PEF generated from the three UMP2/6-31G(d) solutions for CuO^+: (□) solution A; (▼) solution B; (×) solution C.

Table 1
ΔH_0^0 (kcal/mol) for $CuO^+ \rightarrow Cu^+ + O$

	A	B	C
HF/6-31G(d)	23.4	17.9	17.1
MP2(full)/6-31G(d)	25.8	45.1	−19.2
QCISD/6-31G(d)	47.4	87.0	−7.3
B3LYP/6-31G(d)	75.9	85.0	5.3
mPW1PW91/6-31G(d)	65.9	73.3	−2.5
MPW1K/6-31G(d)	51.8	53.1	−3.7
mPW1PW91/6-31+G(d,p)	16.2	28.1	−61.8
MPW1K/6-31+G(d,p)	7.4	19.7	−57.7
HF/MG3	−20.0	8.9	−25.8
MP2(full)/MG3	−0.3	18.7	−99.8
QCISD/MG3	5.0	23.1	−67.6
B3LYP/MG3	18.7	30.8	−15.4
mPW1PW91/MG3	15.5	26.9	−23.8
MPW1K/MG3	7.0	19.1	−59.1
G2	−8.4	12.4	−78.1
G2[a]	−8.4	20.3	−78.1
Exp.	37.4 ± 3.3[b]		
	31.1 ± 2.8[c]		

[a] QCISD energy replaces QCISD(T) energy when QCISD(T) energy is higher.
[b] Ref. [1].
[c] Ref. [4].

Table 2
Equilibrium bond distances (in Å) for CuO^+

	A	B	C
HF/6-31G(d)	1.750	2.019	2.537
MP2(full)/6-31G(d)	1.707	1.633	2.326
QCISD/6-31G(d)	1.697	1.853	2.410
B3LYP/6-31G(d)	1.685	1.673	2.326
mPW1PW91/6-31G(d)	1.688	1.672	2.340
MPW1K/6-31G(d)	1.701	1.693	2.365
mPW1PW91/6-31+G(d,p)	1.762	1.791	2.463
MPW1K/6-31+G(d,p)	1.787	1.882	2.471
HF/MG3	1.759	2.251	2.498
MP2(full)/MG3	1.669	1.916	2.349
QCISD/MG3	1.770	1.788	2.455
B3LYP/MG3	1.771	1.797	2.453
mPW1PW91/MG3	1.768	1.805	2.435
MPW1K/MG3	1.795	1.899	2.440

Table 3
Dipole moment (in D) of CuO^+

	A	B	C
HF/6-31G(d)	6.6	1.6	0.9
MP2/6-31G(d)	5.2	3.6	0.4
B3LYP/6-31G(d)	4.2	3.5	0.3
mPW1PW91/6-31G(d)	4.3	3.5	0.3
MPW1K/6-31G(d)	4.8	3.3	0.5
mPW1PW91/6-31+G(d,p)	3.3	2.2	0.6
MPW1K/6-31+G(d,p)	3.1	1.6	0.7
HF/MG3	6.4	1.5	0.7
MP2/MG3	5.3	1.2	0.4
B3LYP/MG3	3.2	2.3	0.3
mPW1PW91/MG3	3.2	2.2	0.5
MPW1K/MG3	3.0	1.6	0.6

z-axis be the bond axis. The notation we use for the molecular orbitals is the following: the type of orbital (σ, π^*, δ), followed by the two atomic orbitals that dominate the shape of the MO. In solution A, the highest singly occupied orbital is always an antibonding $\pi^*(3d_{xz}2p_z)$ orbital. Solution B has a dipole of 1.2–3.5 D. Solution B has a set of MOs qualitatively similar to solution A. For all methods explored, each orbital and its corresponding energy eigenvalue change in a qualitatively similar manner when going from solution A to B. Because these quantitative changes are slightly different for each method, the actual ordering of the orbitals in solution B varies between the methods investigated. In solution B, the highest singly occupied orbital is always a bonding $\sigma(4s2p_z)$ orbital. Solution C has a dipole of 0.3–0.9 D. Solution C has very high spin contamination for all the methods explored in this paper. The expectation value of the S^2 operator for a pure triplet state would have a value of 2.00, however, for solution C it has a value of ∼3.0 for all methods tested. The six highest occupied β-spin orbitals have little to no spatial similarity to their

α-spin counterparts. Fig. 3 displays the highest singly occupied HF/MG3 molecular orbital for solutions A, B, and C.

For both HF and HDFT, with all basis sets, solution C was found to be an unstable solution that is a saddle point in AO coefficient space. Carefully minimizing the SCF energy from solution C at some internuclear distances yields a stable solution we will call C′. Solution C′ is very similar to solution C; however, it could not be found for most internuclear distances. Because of this, a minimum of energy with respect to internuclear distance could not be found for most methods explored in this paper for solution C′.

For CuH^+, two HF solutions were found for every method and basis set combination studied.
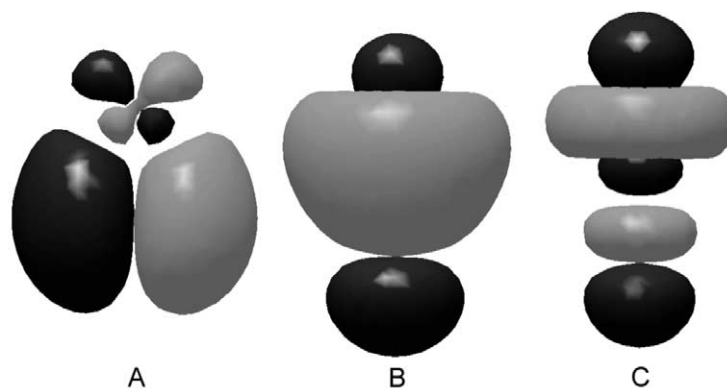
Fig. 3. Plots of the highest singly occupied molecular orbital for UHF/MG3 solutions A, B, and C for CuO^+.

Both solutions are stable in AO coefficient space, and both have expectations of S^2 in the range of 0.75–0.78 for all cases studied, which is reasonably close to the correct value of 0.75. The binding energies and equilibrium geometries for CuH^+ optimized with both solutions are in Tables 4 and 5. For solutions A and B, the highest singly occupied molecular orbital is a $\sigma(4s1s)$ orbital. Solution B has more d_{z^2} character mixed in the highest singly occupied molecular orbital. Fig. 4 displays the highest singly occupied HF/MG3 molecular orbital for solutions A and B.

Only one orbital solution was found for the $CuSi^+$ system; the bond energies and bond distances are given in Table 6. The solution is stable.

Table 4
ΔH_0^0 (in kcal/mol) for $CuH^+ \rightarrow Cu^+ + H$

	A	B
HF/6-31G(d)	43.2	37.9
MP2(full)/6-31G(d)	18.2	8.2
QCISD/6-31G(d)	41.6	27.8
B3LYP/6-31G(d)	67.5	49.2
mPW1PW91/6-31G(d)	58.4	39.2
MPW1K/6-31G(d)	51.6	36.6
mPW1PW91/6-31+G(d,p)	23.0	−17.5
MPW1K/6-31+G(d,p)	17.7	−14.7
HF/MG3	4.9	1.7
MP2(full)/MG3	30.6	12.6
B3LYP/MG3	24.9	−17.8
mPW1PW91/MG3	20.8	−21.1
MPW1K/MG3	15.9	−17.4
G2	−3.6	−34.6
Exp.	21.2 ± 3.0[a]	

[a] Ref. [1].

Table 5
Equilibrium bond distances (in Å) for CuH^+

	A	B
HF/6-31G(d)	1.535	1.577
MP2(full)/6-31G(d)	1.452	1.553
QCISD/6-31G(d)	1.462	1.580
B3LYP/6-31G(d)	1.450	1.546
mPW1PW91/6-31G(d)	1.450	1.544
MPW1K/6-31G(d)	1.454	1.546
mPW1PW91/6-31+G(d,p)	1.488	1.561
MPW1K/6-31G+(d,p)	1.481	1.558
HF/MG3	1.525	2.079
MP2(full)/MG3	1.340	1.470
B3LYP/MG3	1.506	1.574
mPW1PW91/MG3	1.500	1.570
MPW1K/MG3	1.496	1.568
Exp.	1.485 ± 0.015[a]	

[a] Ref. [18].

The G2 method uses the // strategy, and Tables 7 and 8 explore the adequacy of this strategy. The results for all // calculations use SCF solution B for CuO^+ and solution A for CuH^+. Table 7 gives the atomization energy at the MP2(full)/6-31G(d) geometry. Table 8 gives the deviation of the binding energy from experiment.

4. Discussion

The three initial guesses that were used to obtain the three HF/6-31G(d) solutions for CuO^+ all converge on a single solution when used for the HDFT methods. To obtain the three HDFT solu-
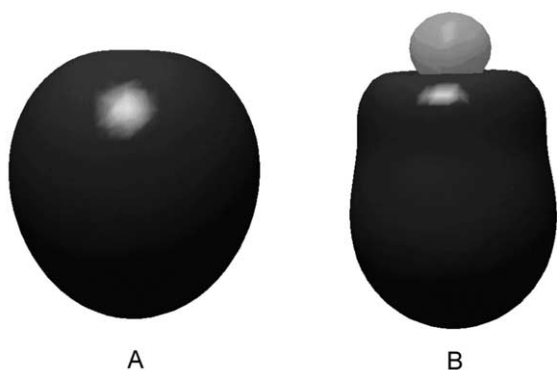
Fig. 4. Plots of the highest singly occupied molecular orbital for UHF/MG3 solutions A and B for CuH^+.

Table 6
Properties of $CuSi^+$

	$CuSi^+ \rightarrow Cu^+ + Si$ ΔH_0^0 (kcal/mol)	$CuSi^+$ Bond length (Å)
HF/6-31G(d)	23.5	2.295
MP2(full)/6-31G(d)	65.9	2.002
B3LYP/6-31G(d)	96.4	2.075
mPW1PW91/6-31G(d)	81.6	2.074
MPW1K/6-31G(d)	63.0	2.089
mPW1PW91/6-31+G(d,p)	58.8	2.243
MPW1K/6-31+G(d,p)	48.4	2.276
HF/MG3	23.5	2.631
MP2(full)/MG3	43.8	2.245
B3LYP/MG3	66.1	2.239
mPW1PW91/MG3	58.1	2.238
MPW1K/MG3	47.8	2.274
G2	59.4	2.002
Exp.	61.1 ± 1.8[a]	

[a] Ref. [4].

Table 7
ΔH_0^0 (kcal/mol) for $CuX^+ \rightarrow Cu^+ + X$ at //MP2(full)/6-31G(d) geometries (kcal/mol)

	CuH^+	CuO^+	$CuSi^+$
MP2(full)/MG3	32.6	10.5	54.1
B3LYP/MG3	24.5	24.8	58.4
mPW1PW91/MG3	20.5	20.9	50.5
MPW1K/MG3	15.7	9.8	38.5
Exp.	21.2 ± 3.0[a]	37.4 ± 3.3[a] 31.1 ± 2.8[b]	61.1 ± 1.8[a]

[a] Ref. [1].
[b] Ref. [4].

Table 8
Absolute deviation of binding energies from experiment (in kcal/mol)

Method	Full optimization	//MP2(full)/ 6-31G(d) Geometry
CuH^+		
MP2(full)/MG3	9.4	11.4
B3LYP/MG3	3.7	3.3
mPW1PW91/MG3	0.4	0.7
MPW1K/MG3	5.3	5.5
CuO^{+a}		
MP2(full)/MG3	15.3	23.5
B3LYP/MG3	3.2	9.2
mPW1PW91/MG3	7.1	13.1
MPW1K/MG3	14.9	24.2
$CuSi^+$		
MP2(full)/MG3	7.3	7.0
B3LYP/MG3	5.0	2.7
mPW1PW91/MG3	3.0	10.6
MPW1K/MG3	13.3	22.6
Average		
MP2(full)/MG3	10.7	14.0
B3LYP/MG3	4.0	5.1
mPW1PW91/MG3	3.5	8.1
MPW1K/MG3	11.2	17.4

[a] Deviations listed in the table are based on an experimental value of 34.0.

tions, the three converged HF/6-31G(d) solutions had to be used as an initial guess. Even then, some HDFT methods converged on the lowest-energy solution, depending on the initial geometry used.

G2 theory performs poorly for both systems where multiple solutions are found to the ground state HF equations and quite well for $CuSi^+$, the one system studied where only one ground-state SCF solution was found. Although using solution B gives the best agreement with experiment for the CuO^+ system, the QCISD(T)/6-311G(d,p) calculation (a component of the G2 energy) gives a higher energy than QCISD/6-311G(d,p). This indicates that the QCISD(T) method is not well-suited for use with this wavefunction. The T_1 diagnostic [33] is an indicator of how good the HF single determinant is at describing the system, and can be used to test the stability of a perturbative connected triples energy contribution, as in the QCISD(T) and CCSD(T) methods. It has been suggested [33] that $T_1 < 0.02$ is desirable when

using the QCISD(T) method, however, the T_1 diagnostics for CuO^+ with the 6-311G(d,p) basis set at the MP2(full)/6-31G(d) geometries are 0.09, 0.09, and 0.01 for solutions A, B, and C, respectively. Because solution B is not well-suited for a QCISD(T) calculation, we also tabulated what the G2 energy would be if we neglect the perturbative connected triples contribution to the energy (equivalent to replacing QCISD(T)/6-311G(d,p) with QCISD/6-311G(d,p) in the G2 energy expression). The use of the MP2(full)/6-31G(d) geometry can also introduce additional errors of several kcal/mol as seen in Table 8. For the case of these CuX^+ systems, the MP2(full)/6-31G(d) geometry is not as reliable as in systems containing atoms from only the first two rows. In addition to problems with the (T) part of the QCISD calculation, Luna and coworkers pointed out that it would be interesting to examine the convergency of the MP perturbation series [34,35] to assess the reliability of the MP2 component of G2.

The previously reported errors in the G2 method come primarily from the choice of the orbitals used in the calculation. For CuH^+, the previously reported G2 binding energies for CuH^+ using the default and the 'stabilized' wavefunctions have very good agreement with the two solutions in the present study, although it is not clear how the wavefunctions were 'stabilized'. For the CuO^+ system, the previously reported binding energy of −78.1 kcal/mol at the G2 level agrees with the G2 energy using solution C in the present study. However, we have found that solution B gives the best agreement with experiment of the three solutions found. Using solution B, G2 has an error of 21.6 kcal/mol. When we neglect the triples calculation, the error is reduced to 13.7 kcal/mol. Although the previous paper claimed that CuO^+ was 'predicted to be unbound at the standard G2 level', a better description might be that CuO^+ is predicted to be unbound using the default GAUSSIAN 98 SCF options.

5. Conclusion

Special attention needs to be paid to the reference wavefunction in copper-containing systems.

For single-level methods, as well as G2, a poor set of orbitals will yield poor results. Although G2 performs better with a good choice of orbitals than with the default orbitals, it is outperformed by the much less expensive HDFT methods mPW1PW91 and B3LYP in agreement with the conclusions of Luna et al. [9]. The underlying problem with G2 calculations on the copper-containing systems studied is the failure of single-reference ab initio methods to give a reasonable description of the system. Finally, the optimal geometry for these simple copper systems varies a great deal between the methods explored. This may make the use of low-level geometries, such as MP2(full)/6-31G(d), an unreliable approximation for these systems.

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