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DFT Calculations for Cu-, Ag-, and Au-Containing Molecules

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The physicochemical properties of a set of molecules containing Cu, Ag, or Au atoms were calculated using the GAUSSIAN program suite, with the purpose of investigating the various density functional theory (DFT) approaches for subsequent application in cluster calculations. The test set comprised the copper-based molecules CuH, CuO, CuS, Cu_2, $CuCl_2^-$, $CuCH_3$, CuC_2H_2, $Cu_2(HCO_2)_4(H_2O)_2$, and $Cu_6H_6(PH_3)_6$ and the silver and gold diatomics AgH, AgO, AgS, Ag_2, AgCu, AuH, AuO, AuS, Au_2, AuCu, and AuAg. The DFT methods used were SVWN, BLYP, and BPW91, together with the DFT hybrids B3LYP and B3PW91. The calculations were carried out with the basis sets LANL2MB, LANL2DZ, 3-21G, and 6-311G (when available). The properties calculated were the molecular geometry, vibrational frequencies, and dissociation energies. It was found that all the DFT-based methods, particularly when allied with the LANL2DZ basis set, produced results which are significantly closer to experimental values than those of the traditional Moller−Plesset (MP2) electron correlation method and which are also applicable to considerably larger molecules. Over the whole test set of molecules, the RMS errors of the four "BX" methods, in conjunction with LANL2DZ, were typically 3−4% for geometries, 6−8% for frequencies, and 10−16% for dissociation energies, with BPW91 and the popular B3LYP at the lower and upper ends of these ranges, respectively, and with the errors being overestimates and underestimates, respectively. The corresponding values for SVWN and MP2 were 2% and 6%, 12% and 12%, and 33% and 42%, with these errors typically being ± and +, + and −, and + and −, with + and − representing overestimates and underestimates, respectively. While the best bond lengths are produced by SVWN (a local spin density approximation), which is not uncommmon, this advantage over the gradient corrected (BX) methods is only slight, and the latter are markedly superior for frequencies and especially dissociation energies. Not supported by the present results are the notions that (all) pure DFT methods underestimate metal−ligand bond lengths and overestimate bond strengths and that hybrid methods are superior (and neither that DFT methods are overcorrelated). Testing on a subset of molecules with BPW91/LANL2DZ revealed no benefit in supplementing this basis set by the addition of diffuse functions, nor of the counterpoise correction. There appear to be specific incompatibilities with some method/basis set combinations, and even the continuing availability of 3-21G for these metals is questionable. Because of its accuracy and reliability, the combination BPW91/LANL2DZ is recommended for these noble-metal systems (and to extensions such as the cluster-model approach to adsorption of a molecule on a metal surface).

1. Introduction

The structure and bonding of molecules to the surfaces of transition and noble metals is of great importance in industry for a number of processes, including corrosion and coatings and heterogeneous catalytic reactions. This has provided a challenge in experimental surface science, computational chemistry, and computational physics to produce accurate predictions of surface processes and reactivity. The theoretical approaches have included methods derived from bulk band-structure calculations and modeling via discrete metal clusters.

Until relatively recently, the ab initio Hartree−Fock (HF) and post-HF "wave function" quantum mechanical calculations were accepted by quantum chemists as the best available methods for computations on molecular systems. Currently, though, these are tending to be superseded by density functional theory (DFT) methods, which originated in work on solids. While the potential advantages of such calculations for diatomics[1] and small metal−atom clusters[2] had been demonstrated much earlier, DFT methods were not widely adopted for molecules until the incorporation of improvements which made them more suitable for these discrete systems.[3] Two considerable influences were the pioneering work of Ziegler[4] on the previously intractable organometallic compounds, and the success of DFT methods on the test set of small molecules already in use by computational chemists.[5,6]

Besides the inherent computational efficiency of DFT, which is beneficial for calculations on any large molecules, is its further advantage of equal applicability anywhere in the Periodic Table,[5] which makes it particularly effective for those molecules involving heavy metal atoms. For some time, however, DFT calculations remained the domain of specialist theoreticians. This changed with the incorporation of DFT methods into the widely used GAUSSIAN[7] suite of programs.

The longer-term objective of the current work is to apply such calculations to cluster models of metal/adsorbate systems. There are, however, many different DFT alternatives available within the GAUSSIAN methodology, and although there have been a number of related studies, including comparisons of different DFT methods on molecules containing the coinage

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metals, these have been far from definitive. They have included studies of copper (and nickel) carbonyls,[8] of the metal dimers,[9] of transition metal hydrides,[10] of some copper-containing molecules[11] (the study most similar to present work), and of cuprous amines and other nitrogen-containing ligands.[12] There is also a review[13] of wave function methods applied to transition metal compounds (including some of copper, silver, and gold). The DFT studies have, however, been rather restricted in scope as to the molecules examined and in the range of methods applied, so it remains unclear which of the DFT alternatives is the most appropriate for the systems of current interest. Hence, in the present investigation, the performance of GAUSSIAN DFT methods are compared both against the standard wave function methods and, more importantly, against experimental data. To achieve this, calculations were carried out on a number of discrete molecules, containing copper, silver, and gold atoms. The choice of molecules is determined by the availability of experimental data and their relevance to experimental systems of interest. In common with various previous calculations, geometries, vibrational frequencies, and dissociation energies were determined, with the accuracy of these results then being used as the criterion for assessing the different methods.

2. Calculational Methods

The calculations were performed mainly with the GAUSSIAN 94 quantum chemistry software package,[7] which has been expanded to include a number of DFT methods, on an IBM RS-6000, though some of the later work was carried out with GAUSSIAN 98 on a 500 MHz Digital Alpha. In both cases, these were multiuser systems, which imposes some constraints on the program operation (job swapping and disk space).

2.1. Theoretical Methods. The two wave function methods used are Hartree−Fock (HF) and Moller−Plesset second order-perturbation theory (MP2). HF is useful in initiating calculations, but our main comparative interest will be in the results of the MP2 method because of its incorporation of electron correlation. (The default version of MP2 was used, which does not include the core electrons in the correlation calculations. A limited number of test results using the full version showed negligible difference to calculated properties. The distinction is, furthermore, quite irrelevant when using basis functions incorporating an effective core potential—see below.)

The various density functional methods available are a combination of exchange functionals and correlational functionals. The exchange functionals used are the original one of Slater (S), also referred to as the local spin density (LSD) exchange, and the update of Becke (B), which incorporates the Slater exchange along with density-gradient corrections. The correlation functionals used are (1) the original of Vosko, Wilk, and Nusair (VWN), often referred to as LSD correlation, (2) the widely used one of Lee, Yang, and Parr (LYP), which includes both local- and nonlocal-density terms, and (3) the subsequent one of Perdew and Wang (PW91 = PW), another gradient-corrected functional [and recommended over the earlier version of Perdew (P86) by the latter]. The PW functional, in particular, seems to have been somewhat "underemployed", even though it has the notional advantage of satisfying to a wider range of theoretical constraints than other functionals.[14] Of the six resulting possibilities, the pure DFT models chosen are the combinations SVWN (LSD approximation), BLYP, and BPW (both generalized gradient approximation, GGA, methods), which could be expected to be both "balanced" (as between exchange and correlation) and to show increasing sophistication.

There are also hybrid methods available, which include a combination of Hartree−Fock exchange and DFT exchange correlation. The ones chosen are Becke's three-parameter hybrid method (B3), in combination with either LYP (B3LYP) or PW (B3PW). All four methods based on Becke's exchange functionals (BLYP, BPW, B3LYP, and B3PW) are referred to collectively as the BX methods.

These methods are selected because, on one hand, they "make connection" with earlier studies (SVWV, BLYP, and B3LYP) and, on the other, they are some of the most advanced methods available (BPW, B3LYP, and B3PW). In addition, all have been used with some success in previous studies and should be suitable for the type of system under investigation. Also though, there have been repeated comments[8a,11] relating to deficiencies in pure DFT methods (collectively), which, while they may have been true of the original LSDA calculations, do not seem to be clearly substantiated by GGA results, and advantages mooted for the hybrid methods,[8b] in particular B3LYP, without it being clear that there have been adequate comparisons with other, correspondingly advanced methods. It is pertinent to investigate whether these claims hold for this group of metal-containing molecules.

2.2. Basis Sets. For the heavier atoms, the choice here is quite restricted, with the traditional, all-electron, split-valence basis sets being limited to the double-ζ 3-21G[15] and the triple-ζ 6-311G[16] even for midrange elements (and none for the heaviest atoms). While the latter were purposely developed for atoms up to Br, the former, originally useful for lighter atoms, were also extended specifically to include the first transition series,[17] and further up to Xe, although without confidence that these are adequate for the heaviest atoms.

By contrast, the LANL[18] basis sets were developed for atoms of high atomic number. The core basis functions are replaced by an effective core potential (ECP). Whereas the initial version retained only the valence orbitals explicitly, the more recent version, LANL2, retains some of the outer-core functions when applied to third- and higher-row atoms. The LANL basis sets are available either as minimum basis (MB) or double-ζ (DZ). The abbreviations L2MB and L2DZ will be used to denote these two basis sets. For first row atoms (for which there is no LANL ECP), GAUSSIAN utilizes the all-electron minimum and double-ζ bases STO-3G and D95.

The basis sets utilized for copper are thus L2MB, L2DZ, 3-21G, and 6-311G; for silverm L2MB, L2DZ, and 3-21G; and for goldm only L2MB and L2DZ. Even for copper, the number of basis functions in the relatively crude 3-21G (29) well exceeds those of the quite-sophisticated 6-311G for a light atom such as oxygen (13). It is for this reason that ECPs are employed for the heavier atoms (22 basis functions for L2DZ for Au). It may also be noted that there could, in principle, be a slight complication when comparing results from the all-electron and LANL basis sets, since (the ECPs of) the latter incorporate relativistic effects (for the heavier atoms), whereas the former do not. In practice, however, while we have indeed experienced difficulties with 3-21G, these are not due to such effects, which are small for Ag and negligible for Cu[19].

What we have not done is employ "purposely tailored" basis sets, unique to each element, such as has been done in some earlier DFT calculations on copper-containing molecules.[8b] Although these might have some advantages (particularly as regards basis set completeness), we regard this as outside the spirit of GAUSSIAN, which incorporates basis sets which apply to a whole range of elements and which are accessible to all users. More importantly and as will be demonstrated, large basis sets become intractable even for discrete molecules and are quite unsuitable for extension to clusters.

TABLE 1: RMS % Errors for Calculated Geometric Parameters

basis set/method	HF	MP2	SVWN	BLYP	BWP	B3LYP	B3PW	basis set error
(a) Small Copper-Containing Molecules: CuH, CuO, CuS, Cu_2, $CuCl_2^-$, $Cu-CH_3$								
L2MB	11	11	4	7	7	8	7	8
L2DZ	9	6	**2**	4	4	4	4	5
3-21G	7	8	10	8	8	9	9	8
6-311G	8	4	**2**	3	3	3	**2**	**4**
method error	9	7	**5**	6	**5**	6	6	6
(b) Silver Diatomics: AgH, AgO, Ag_2								
L2MB	8	8	3	6	5	6	6	6
L2DZ	7	5	3	**2**	**2**	**2**	**2**	**3**
3-21G	7	5	5	3	3	3	3	4
method error	7	6	**4**	**4**	**4**	**4**	**4**	5
(c) Gold Diatomics: AuH, Au_2								
L2MB	8	8	4	7	6	7	6	7
L2DZ	5	5	**1**	4	3	3	**3**	**3**
method error	6	6	**3**	5	5	5	4	5
(d) Large Copper-Containing Molecules: $Cu_2(HCO_2)_4$, $Cu_6H_6(PH_3)_6$								
L2MB	10	*9*[a]	6	7	7	7	7	8
L2DZ	9	*9*[a]	6	6	6	6	6	***7***
3-21G[a]	***5***	*16*	*9*	*9*	*9*	*8*	*8*	*9*
6-311G[a]	*6*	*b*	*8*	*7*	*7*	*7*	*7*	*7*
method error	***7***	*11*	***7***	***7***	***7***	***7***	***7***	7

experimental values for the small molecules given in subsequent tables and for the two large molecules are as follows:

$Cu_2(HCO_2)_4$		ref 18b		$Cu_6H_6(PH_3)_6$	ref 19				
r(CuCu)	r(CuO)	a(CuCuO)	a(OCO)	$r(Cu_aCu_{b'})$	$r(Cu_aCu_b)$	r(PCu)	$a(PCu_aCu_{b'})$	$a(PCu_aCu_b)$	$a(PCu_aCu_{a'})$
2.64 Å	1.97 Å	83°	112°	2.655 Å	2.54 Å	2.24 Å	129.6°	139.7°	172.0°

[a] Results for $Cu_2(HCO_2)_4$ only. [b] Insufficient disk capacity.

2.3. Calculation of Errors. To compare the various method and basis set combinations, the results have been presented in the form of an error analysis. Percentage errors in the calculated values of the parameters—bond lengths and angles, vibrational frequencies and dissociation energies—were found by comparison with experimental data.

For each calculated parameter (x), we define the percentage error, ϵ, as

$$\epsilon_x = \left\{\frac{x_{\text{calc}} - x_{\text{exptl}}}{x_{\text{exptl}}}\right\} \times 100$$

The root mean square (RMS) error is then calculated from the percentage errors of a given set of molecules, for each method/basis set combination within each set of parameters

$$\text{RMS\% Error } \xi_x = \sqrt{\frac{w_1\epsilon_1^{\,2} + w_2\epsilon_2^{\,2} ... + w_n\epsilon_n^{\,2}}{n}}$$

where n = number of parameters (e.g., the 3 vibrational frequencies for a triatomic molecule) and w = weighting factor. The value of w is usually unity but in some cases is smaller. This is illustrated by $CuCH_3$, which has six vibrations, which can be compared with experimental values (Table 4). The four highest wavenumber values, which constitute vibrations within the methyl group, are considered to be less significant (in the present context) than the other two which involve the copper, and so, have each been given a weighting of 0.25 (thus yielding an effective $n = 3$).

3. Results and Discussion

The RMS percentage errors for each method/basis set combination are gathered together in subsets of the 20 molecules and presented in the following sections for geometry, vibrational frequencies, and dissociation energies. The experimental data used in this comparison are listed in the results Tables.

3.1. Geometry. Bond lengths and angles are the molecular parameters which have proved easiest to calculate accurately, and for molecules containing first-row atoms, satisfactory results are achieved even with HF. Molecules containing metal atoms have, however, been recognized as a distinctly greater challenge, so it is interesting to see how the various DFT methods perform (along with HF and MP2).

Table 1a groups together the RMS errors for the small molecules containing copper, which include CuH, CuO, CuS, Cu_2, $CuCl_2^-$, and $CuCH_3$, using all four basis sets. Within this set of molecules, the SVWN and BPW methods yield the most accurate geometries (mainly bond lengths) overall, followed closely by the other pure and hybrid DFT methods. Here the wave function methods are the least accurate. The best basis set, overall, is the 6-311G, closely followed by the L2DZ. For the specific method/basis set combination, the best performances are shown by SVWN/L2DZ, SVWN/6-311G, and B3PW/6-311G, although all of the pure or hybrid DFT methods give very acceptable results with these two basis sets.

Table 1b contains the results for the silver diatomics, AgH, AgO, and Ag_2. Generally the errors are surprisingly low, although the BX methods coupled with L2DZ are in better agreement than the remaining combinations.

The results for the gold diatomics, AuH, Au_2, are shown in Table 1c. Here L2DZ is clearly superior to L2MB (the only two basis sets available for gold), with the best agreement occurring in combination with SVWN.

Last, Table 1d illustrates the results of a study undertaken of two much larger copper-containing molecules, $Cu_2(HCO_2)_4$ and $Cu_6H_6(PH_3)_6$. In both cases, the molecules are “simplified” versions of those for which experimental data is available to make them computationally tractable. The dicopper tetraformate, of D_{4h} symmetry, with the formates bridging the two axial

TABLE 2: Errors in Bond Lengths, LANL2DZ Basis Set

		HF		MP2		SVWN		BLYP		BPW		B3LYP		B3PW	
molecule	exptl r/Å[a]	Å	%	Å	%	Å	%	Å	%	Å	%	Å	%	Å	%
CuH	1.463	0.113	8	0.076	5	0.005	0	0.030	2	0.030	2	0.035	2	0.036	2
CuO	1.724	0.173	10	0.130	8	−0.005	0	0.055	3	0.050	3	0.079	5	0.077	4
CuS	2.051	0.221	11	0.171	8	0.056	3	0.120	6	0.107	5	0.130	6	0.121	6
Cu_2	2.220	0.201	9	0.110	5	−0.057	−3	0.029	1	0.019	1	0.042	2	0.035	2
$CuCl_2^-$	2.090[b]	0.188	9	0.133	6	0.060	3	0.135	6	0.123	6	0.126	6	0.118	6
$Cu-CH_3$	1.866[c]	0.144	8	0.092	5	−0.012	−1	0.058	3	0.044	2	0.060	3	0.051	3
AgH	1.618	0.102	6	0.088	5	−0.013	−1	0.023	1	0.017	1	0.027	2	0.023	1
AgO	2.003	0.107	5	0.065	3	−0.116	−6	−0.031	−2	−0.042	−2	−0.003	0	−0.010	0
Ag_2	2.530	0.200	8	0.151	6	−0.029	−1	0.088	3	0.056	2	0.082	3	0.060	2
AuH	1.524	0.064	4	0.059	4	0.019	1	0.040	3	0.031	2	0.035	2	0.029	2
Au_2	2.472[d]	0.143	6	0.132	5	0.014	1	0.116	5	0.080	3	0.102	4	0.075	3
sign		+*ve*		+*ve*		±*ve*		+*ve*		+*ve*		+*ve*		+*ve*	
RMS		0.158	8	0.115	6	0.048	2	0.077	4	0.064	3	0.077	4	0.068	3

[a] All values from Huber and Herzberg,[35] except the following: (*b*) ref 36b, (*c*) ref 36d, (*d*) ref 9a.

TABLE 3: RMS % Errors of Calculated Vibrational Frequencies[a]

basis set/ method	HF	MP2	SVWN	BLYP	BPW	B3LYP	B3PW	basis set error
(a) Copper Diatomics (CuH, CuO, CuS, Cu_2)								
L2MB	23	24	8	16	16	18	19	18
L2DZ	18	12	10	5	4	8	7	9
3-21G	33	40	61	51	50	53	52	49
6-311G	22	12	13	4	4	4	4	9
method error	24	22	23	19	18	21	20	21
(b) Small Copper Molecules ($CuCl_2^-$, $CuCH_3$, CuC_2H_2)								
L2MB	43	31	41	29	30	36	37	35
L2DZ	32	37	33	28	29	28	29	31
3-21G	56	53	67	60	61	57	57	59
6-311G	35	51	37	35	36	35	36	38
method error	42	43	45	38	39	39	40	41
(c) Silver Diatomics (AgH, AgO, Ag_2, AgCu)								
L2MB	22	23	9	18	18	21	22	19
L2DZ	17	12	15	7	4	6	5	9
3-21G	20	19	30	15	14	11	21	19
method error	20	18	18	13	12	13	16	16
(d) Gold Diatomics (AuH, Au_2, AuCu)								
L2MB	23	24	10	21	19	20	18	19
L2DZ	17	13	6	12	9	11	9	11
method error	20	19	8	17	14	15	13	15

[a] G94 and G98 sometimes give small frequency differences, but these are insignificant in the error calculations.

coppers, has been shown to exist by spectrophotometry data but has not been isolated and characterized.[20] Experimental data are available for the more widely studied dicopper tetraacetate dihydrate,[21] and our calculations are compared with this complex, which could confidently be expected to have a similar geometry. Likewise, the hexanuclear complex, phosphinocopper(I) hydride cluster $Cu_6H_6(Pph_3)_6$, which has been characterized by X-ray diffraction,[22] has been modeled by $Cu_6H_6(PH_3)_6$. These molecules have D_{3d} symmetry, with two staggered equilateral triangles of copper atoms (a,b,c; a′,b′,c′); the phosphines are bonded radially to the coppers, and the hydrogens are located “internally”. Because the molecules studied are significantly different than the systems for which we have experimental data, there is less certainty in the error results, compared with our other calculations. What is interesting for us to note, however, is how well the various methods and basis sets cope, as large molecules do introduce a significant degree of complexity into the calculations, particularly the copper−phosphine molecule, with its large number of copper atoms.

Table 1d illustrates some of the technical difficulties encountered. It can be seen that only the ECP basis sets (L2MB and L2DZ) could be used for the copper−phosphine molecule. The MP2 method when combined with the large 6-311G basis set, also proved intractable for the calculations not only on the copper−phosphine molecule, but also for the copper−formate molecule. In each case, neither of the calculations ran to completion because they exceeded the available disk capacity of the computer. The geometric parameters of the copper−formate are the bond lengths *r*(CuCu) and *r*(CuO) and the bond angles *a*(CuCuO) and *a*(OCO) and, for the copper−phosphine, $r(Cu_aCu_{b'})$, $r(Cu_aCu_b)$, *r*(PCu), $a(PCu_aCu_{b'})$, $a(PCu_aCu_b)$, and $a(PCu_aCu_{a'})$. Because the calculated values in Table 1d are not true representations of the experimental models, these results cannot be considered to be as accurate as in the previous tables. It is still worthwhile, however, to draw the comparison, as the calculations are large and do represent a significant challenge to the computational methodologies. Although the HF/3-21G combination does display the lowest number, this is derived only from the single molecule, and on the whole, the density functionals and hybrids, combined with the L2DZ basis set, show an encouraging and reliable outcome.

Overall, the predictions of geometric structure by the density functionals and the hybrids, coupled with the L2DZ basis set, showed good consistency, better agreement with experimental values than the other combinations of methods and basis sets, and the reliability to extend to large molecules.

While the RMS errors give a good overview of the general performance of each of the methods and basis sets, they do not indicate whether the calculations are under- or overestimates. In view of claims[8a] that DFT approaches usually underestimate metal−ligand bond lengths [in contrast to the wave function methods] and that standard GGA functionals tend to give bond lengths that are too short [in contrast with the B3LYP hybrid approach], it is pertinent to examine the actual bond-length errors for the present set of molecules. These are presented in Table 2 (L2DZ basis set). While HF and MP2 exhibit the expected overestimate (positive errors), the BX methods also overestimate (though to a substantially lesser extent), and even for SVWN, the number of underestimates is closely matched by overestimates. As well, there is no significant difference between the pure GCA functionals and their hybrid counterparts, and in fact, the performance of B3LYP is marginally worse than BPW. It would appear that, for this group of metals (and ligands), the previous claims are unsupported.

3.2. Vibrational Frequencies. Frequency calculations using the HF level of theory are generally known to contain systematic errors, and it is usual practice to scale down the frequencies to

TABLE 4: % Errors of Calculated Vibrational Frequencies of $CuCl_2^-$, $CuCH_3$, and CuC_2H_2

vibration	basis set/method	HF	MP2	SVWN	BLYP	BPW	B3LYP	B3PW
			$CuCl_2^-$					
$\nu(CuCl_2^-)$ degen bend	L2MB	−20	−20	−1	−15	−13	−12	−11
109 $cm^{-1\,a}$	L2DZ	−22	−10	0	−9	−7	−8	−7
	3-21G[b]	−82	*4*	*36*	*26*	*27*	*6*	*5*
	6-311G	−8	14	22	13	15	13	14
$\nu(CuCl_2^-)$ sym str	L2MB	−17	−17	−1	−12	−11	−10	−10
300 $cm^{-1\,a}$	L2DZ	−19	−9	2	−8	−7	−7	−7
	3-21G[b]	−1	*11*	*24*	*18*	*16*	*14*	*12*
	6-311G	−27	−14	−1	−12	−10	−11	−10
$\nu(CuCl_2^-)$ asym str	L2MB	−10	−9	4	−6	−5	−4	−3
[a]405 cm^{-1}	L2DZ	−11	1	11	−2	0	0	1
	3-21G[b]	−10	*1*	*5*	*1*	*−1*	*−1*	*−2*
	6-311G	−20	−9	2	−10	−8	−8	−7
			$CuCH_3$					
$\nu(CuC)$ sym str	L2MB	33	26	67	45	47	46	48
350 $cm^{-1\,c}$	L2DZ	40	46	72	52	56	52	55
	3-21G	105	108	143	127	128	124	124
	6-311G	41	70	81	64	69	66	69
$\nu(CuCH_3)$ degen rock	L2MB	76	63	74	70	71	73	74
424 $cm^{-1\,c}$	L2DZ	59	59	62	61	62	63	63
	3-21G	72	73	68	67	69	73	73
	6-311G	66	75	69	72	72	73	72
$\nu(CH_3)$ sym def	L2MB	19	8	5	4	5	8	9
1196 $cm^{-1\,c}$	L2DZ	4	−2	−7	−7	−6	−4	−3
	3-21G	22	18	14	15	15	17	17
	6-311G	9	10	2	3	3	5	5
$\nu(CH_3)$ degen def	L2MB	34	23	15	16	16	20	20
1336 $cm^{-1\,c}$	L2DZ	20	12	5	7	7	10	10
	3-21G	19	12	2	5	5	9	9
	6-311G	20	11	5	8	7	11	10
$\nu(CH_3)$ sym str	L2MB	21	13	10	8	9	12	12
2929 $cm^{-1\,c}$	L2DZ	8	3	2	1	2	4	4
	3-21G	8	5	−1	−1	−1	3	3
	6-311G	7	2	0	0	0	2	3
$\nu(CH_3)$ asym degen str	L2MB	30	21	18	16	17	20	21
2880 $cm^{-1\,c}$	L2DZ	13	9	8	7	8	10	10
	3-21G	12	9	2	2	2	6	6
	6-311G	11	7	5	4	5	7	8
			CuC_2H_2[d]					
$\nu(CuC)$ str	L2MB	**−80**	*e*	*e*	−14	−14	*e*	*e*
380 $cm^{-1\,f}$	L2DZ	*e*	**−77**	26	10	15	−5	−4
	3-21G	70	89	*e*	*e*	*e*	*68*	*68*
	6-311G	vdw	**−51**	17	32	35	32	36
$\nu(CC)$ str	L2MB	**29**	*e*	*e*	−2	0	*e*	*e*
1870 $cm^{-1\,f}$	L2DZ	*e*	6	−8	−11	−11	−9	−9
	3-21G	0	**−6**	*e*	*e*	*e*	*−6*	*−5*
	6-311G	vdw	**79**	−8	−12	−12	−10	−11
$\nu(CH)$ str	L2MB	**28**	*e*	*e*	12	13	*e*	*e*
3040 $cm^{-1\,f}$	L2DZ	*e*	**15**	6	6	6	9	9
	3-21G	*17*	**11**	*e*	*e*	*e*	*11*	*10*
	6-311G	vdw	**59**	5	4	4	6	6

[a] From ref 36c. [b] Values in italics = bent. [c] From ref 36e. [d] Values in roman, lightface = C_s symmetry. Values in italics = C_s and C_{2v}. Values in bold = C_{2v}. vdw = van der Waals. [e] No result. [f] From ref 21.

achieve agreement with experimental values.[23a] Post-HF calculations, which include electron correlation, give more accurate predictions but are limited when applied to larger molecules, or those systems containing metals, because of the high computational requirements. The DFT and hybrids provide a possible means of performing these calculations economically and with reasonable accuracy.

Table 3a contains the calculated errors for the copper diatomics, CuH, CuO, CuS, and Cu_2. Within this group, the best agreement is found with the methods BPW and BLYP combined with L2DZ and also with all the BX methods with the 6-311G basis set. The errors produced by MP2 are somewhat higher, and indeed comparable, to those of HF. Even more striking than the differences between the methods are those between the basis sets, with the 3-21G performing particularly poorly.

The results for a group of small copper molecules, $CuCl_2^-$, $CuCH_3$, and CuC_2H_2, are shown in Table 3b. The much larger errors which can be seen in this study are principally associated with poor predictions of those vibrations representing the copper−carbon modes, as will be subsequently discussed.

Table 3c shows the results for the silver diatomics, AgH, AgO, Ag_2, and AgCu. The 6-311G basis set is not available for silver. While the frequency predictions of BPW/L2DZ are in closest agreement with experimental results, those of all the BXs combined with the L2DZ basis set performed significantly better than the other combinations.

The errors for the gold diatomics are given in Table 3d. Only the two ECP basis sets are available for use with gold, and once again, L2DZ is the better performer. Here the SVWN predictions are clearly closest to experimental values, followed by B3PW and BPW.

Altogether, the predictions of the pure DFT's and hybrids for the vibrational frequencies are in consistently good agreement with the experimental values (except for CuC) and generally outperform the MP2 and HF methods. From the RMS

TABLE 5: Errors in Vibration Frequencies, LANL2DZ Basis Set

molecule	exptl	HF		MP2		SVWN		BLYP		BPW		B3LYP		B3PW	
	cm^{-1} [a]	cm^{-1}	%	cm^{-1}	%	cm^{-1}	%	cm^{-1}	%	cm^{-1}	%	cm^{-1}	%	cm^{-1}	%
CuH	1941	−264	−14	−176	−9	−12	−1	−112	−6	−108	−6	−118	−6	−118	−6
CuO	640	−80	−12	−71	−11	77	12	−30	−5	−27	−4	−65	−10	−65	−10
CuS	415	−72	−17	−48	−12	14	3	−30	−7	−22	−5	−41	−10	−35	−8
Cu_2	265	−66	−25	−36	−14	46	17	−7	−3	−1	0	−12	−5	−9	−3
AgH	1760	−183	−10	−164	−9	75	4	−62	−4	−33	−2	−55	−3	−36	−2
AgO	490	−31	−6	−20	−4	122	25	−18	−4	−8	−2	−31	−6	−27	−5
Ag_2	192[b]	−43	−22	−29	−15	24	12	−21	−11	−11	−6	−18	−9	−11	−6
AgCu	232[c]	−56	−24	−38	−16	27	12	−14	−6	−9	−4	−15	−6	−11	−5
AuH	2305	−276	−12	−298	−13	−135	−6	−217	−9	−203	−9	−194	−8	−186	−8
Au_2	191	−34	−18	−23	−12	2	1	−33	−17	−23	−12	−28	−14	−20	−11
AuCu	250[c]	−49	−20	−34	−13	19	8	−22	−9	−14	−6	−22	−9	−16	−6
sign		−*ve*		−*ve*		(+*ve*)		−*ve*		−*ve*		−*ve*		−*ve*	
RMS		137	17	126	12	70	12	82	8	75	6	79	8	75	7

[a] All values from ref 35, except the following: (*b*) ref 9a and (*c*) ref 36a.

errors, there is no justification for selecting B3LYP ahead of any of the other BX methods, but BPW does have a slight edge. Even more striking is the difference between the basis sets, with 3-21G clearly being the worst and L2DZ the best (together with 6-311G, when available).

Returning to the small copper molecules, the percentage errors for each of the individual vibrational modes for each of the three molecules are shown in Table 4.

For $CuCl_2^-$, the errors are quite modest, and all the calculations predict the experimental linear geometry, with the exception of the 3-21G basis set which yields a bent geometry with all the methods except HF. [The original 3-21G calculations with the electron correlation methods each predicted imaginary values for the low-frequency degenerate Cu−Cl bending mode, indicative of a transition state. The calculations were redone with a lower symmetry, and the results for 3-21G in Table 4 correspond to the resulting frequencies of the bent molecule. The bond angle varied between 161° and 165° for the different methods.] For each mode, L2DZ is better than 6-311G, and while HF is clearly inferior, there is not much to choose between the other methods.

The highest errors can be seen in $CuCH_3$, with the large overestimation (positive errors) of the CuC symmetric stretch and the $CuCH_3$ degenerate rock, for all methods and basis sets. This suggests that there is an underlying problem in the representation of copper−carbon bonding in this molecule with all the method/basis set combinations used here. The predictions of the remaining frequencies show the usual, much better, agreement with the experimental results. For these modes, 6-311G is marginally superior to L2DZ, and SVWN, BLYP, and BPW are marginally superior to the other methods.

The other small molecule with a Cu−C bond and an assigned vibrational spectrum[24] is CuC_2H_2. From ESR studies,[25] it was inferred that, unlike the Al and Ag analogues, which both have a σ-bonding vinyl structure, the Cu forms a π-complex. Within our calculations on CuC_2H_2, using a number of method/basis set combinations, both geometries were found: the π-bonding structure with C_{2v} symmetry, inferred from the experimental ESR studies, and the planar trans vinyl structure with C_s symmetry. Most of the calculations which optimized with C_{2v} symmetry also produced an imaginary frequency, indicating a transition state. The MP2 method did, however, consistently produce a stable minimum with this geometry. The DFT methods all yielded a minimum for the C_s structure—as has also been found previously.[26] From the frequency percentage errors contained in Table 4, it can be seen that the resulting vibrational wavenumbers for the C_s structure are in closer agreement with the experimental infrared values than are those obtained from the C_{2v} geometry. While in part this may be due to the inferiority of the MP2 method rather than the C_{2v} geometry per se, the errors well exceed those of the previous molecules, which points to the geometry (rather than the method) as the major cause of the discrepancy. The smaller errors and the consistency of the density functional methods suggest that they provide the most accurate model. The failures of L2MB and 3-21G suggest insufficient flexibility with these basis functions. Somewhat surprising, in view of the corresponding $CuCH_3$ results, are the relatively small errors with BX/L2DZ for the Cu−C stretch. Obviously, the representation of copper−carbon bonding with this basis set is not always problematic.

Again, it is worthwhile looking past the RMS errors to see whether the calculations are under- or over-estimates. The actual frequency errors (in both cm^{-1} and %) for all the diatomics are presented in Table 5 (L2DZ basis set). While SVWN exhibits predominantly overestimates (positive errors), all the rest yield underestimates, with the four BX methods yielding similar and clearly superior results. Again, there is essentially no difference between the pure GCA functionals and their hybrid counterparts, though the performance of BPW is marginally better than the much-favored B3LYP.

These conclusions vis a viz these methods, and in particular the nonsuperiority of B3LYP, and the slight edge of BPW, are somewhat contrary to the "perceived wisdom", which seems to cede the "frequencies" crown to B3LYP (eg[23a]). One of the more extensive studies was that of Rauhut and Pulay,[27] who examined a total of 31 organic molecules with 644 frequencies. The scaling factors which they obtained (to apply to the calculated values to bring them into line with experiment) for BLYP and B3LYP with a 6-31G* basis set, along with those for HF and MP2, are included in Table 6, together with those for the present group of molecules, obtained for the various methods using the L2DZ basis set. These scaling factors correspond to the Slopes of the least-squares-best-fit straight line and, for the present data, the corresponding Intercepts are also included. With all the present molecules included, the two sets of scaling factors are very similar, with BLYP and BPW giving the best results. Without the $CuCH_3$ values, however, the scaling factors all change from less to greater than unity. Clearly, there can be large variations between different classes of molecules, and there should be no assumption that the calculated frequencies (by any method) are always overestimates. There is also no superiority of B3LYP over the other BX methods.

3.3. Dissociation Energy. While on one hand the HF method is known to generally underestimate dissociation energies (eg[23b])

TABLE 6: Scaling Factors for Calculated Vibrational Frequencies

compounds	HF	MP2	SVWN	BLYP	BPW	B3LYP	B3PW
organics	0.89	0.95		0.995		0.963	
ref 24		quoted "standard" values				31 mols, 644 freqs; 6-31G*	
all Table 3	0.94	0.98	0.99	0.99	0.99	0.97	0.97
intercept	57.62	19.38	−50.84	−0.32	−5.42	12.35	9.43
Table 3 excl $CuCH_3$	1.13	1.13	1.03	1.07	1.07	1.07	1.06
intercept	14.62	−9.58	−47.43	−4.12	−9.11	2.75	−0.49

TABLE 7: RMS % Errors of Calculated Dissociation Energies[a]

basis set	method							basis set error
	HF	MP2	SVWN	BLYP	BPW	B3LYP	B3PW	
(a) Copper Diatomics (CuH, CuO, CuS, Cu_2)								
L2MB	105	75	30	17	17	25	30	43
L2DZ	69	30	34	9	**6**	8	10	**24**
3-21G	75	200	100	59	60	62	98	93
6-311G	70	44	60	42	30	17	61	46
method error	80	87	56	31	**28**	**28**	50	51
(b) Silver Diatomics (AgH, AgO, AgS, Ag_2, AgCu)								
L2MB	126	111	39	**20**	46	31	37	59
L2DZ	99	61	38	29	31	36	51	49
3-21G[b]	84	82	*23*	*30*	*32*	*38*	51	49
method error	103	85	33	**26**	36	35	46	52
(c) Gold Diatomics (AuH, AuO, AuS, Au_2, AuCu, AuAg)								
L2MB	102	74	28	21	23	29	32	44
L2DZ	80	39	28	**12**	**12**	20	20	**30**
method error	91	56	28	**16**	**17**	25	26	37

[a] Calculated D_e's related to experimental D_0's via $D_e = D_o + hc\omega/2$. [b] For AgCu, the 3-21G basis set did not converge when combined with the italicized methods.

TABLE 8: % Errors of Calculated Dissociation Energies of Copper Diatomics

molecule	basis set	HF	MP2	SVWN	BLYP	BPW	B3LYP	B3PW
CuH	L2MB	−42	−27	47	26	18	17	10
	L2DZ	−53	−30	18	2	−3	−3	−7
	3-21G	53	123	11	−12	−11	−34	−34
	6-311G	−51	−17	40	32	22	19	−12
CuO	L2MB	−171	−112	33	5	−8	−29	−39
	L2DZ	−85	−27	44	11	7	−8	−12
	3-21G	65	200	167	112	112	56	166
	6-311G	−85	−63	79	48	41	19	121
CuS	L2MB	−79	−66	5	−19	−21	−29	−30
	L2DZ	−58	−34	22	−7	−5	−14	−13
	3-21G	36	151	78	33	39	−2	3
	6-311G	−57	−27	51	30	25	9	7
Cu_2	L2MB	−85	−69	16	−7	−18	−23	−31
	L2DZ	−75	−27	44	12	7	−1	−5
	3-21G	120	286	77	2	13	−105	−98
	6-311G	−82	−53	64	52	30	17	1

because of its neglect of electron correlation, on the other it is recognized (eg[28]) that the LSDA-DFT tends to overbinding because it underestimates the exchange-correlation contribution in regions of low electron density, which are more extensive for the atoms when separate than when combined into a molecule. It is thus of considerable interest to see to what extent this behavior is rectified by the MP2 and GGA-DFT methods, in reproducing the dissociation energies of diatomic molecules containing copper, silver and gold.

The RMS percentage errors for the dissociation energy of the copper diatomics, CuH, CuO, CuS, and Cu_2 are contained in Table 7a. These mostly show much larger values than those for the geometries and vibrational frequencies. There are also very large differences in the error values, with a good performance from the L2DZ basis set, particularly when combined with the BX methods. BPW and B3LYP are the most reliable methods overall, with the BPW/L2DZ combination giving the most accurate predictions. There seems to be an incompatibility between the DFT methods and the all-electron basis sets, with some very large errors occurring. Not unexpectedly, the errors with SVWN are consistently larger than those of BX.

Table 7b summarizes the RMS errors for the silver diatomics, AgH, AgO, AgS, and AgCu. All the errors are substantially larger, with little difference between L2MB and L2DZ for the DFT methods. (Within this group, the 3-21G basis set actually appears to be quite a good performer, but the results are somewhat distorted by the fact that it did not converge for AgCu when combined with the DFT-based methods.) The BLYP method produced the results closest to experimental data.

The results for the gold diatomics, AuH, AuO, AuS, Au_2, AuCu, and AuAg are listed in Table 7c. Only the LANL2 basis sets are available for comparison, but the L2DZ basis provides the better performance, and BLYP and BPW are the most accurate methods. The lowest individual errors are also achieved by L2DZ combined with BLYP and BPW.

Overall, the DFT methods are all superior to MP2, and within the former, BLYP and BPW performed marginally better than the other three. The same observations remain true when the basis set is confined to L2DZ, which is the most reliable. The corresponding combinations thus represents the most consistent and efficient method for calculating the dissociation energies of these molecules.

The actual percentage errors for the copper diatomics are shown in Table 8. As expected, all the HF values (except for 3-21G) are negative, confirming the anticipated underestimate of the dissociation energy. For MP2, they are all numerically smaller (again except for 3-21G) but still negative, suggesting a partial allowance for electron correlation. The fact that the 3-21G errors with MP2 are more than double those with HF must surely indicate the unsuitability of this basis set for these systems. For the DFT methods, while the errors for SVWN are indeed all positive (indicating a systematic overestimate, as anticipated), those for BLYP and BPW (plus the two B3s) are almost equally divided, both overall and for the markedly superior L2DZ basis set. At least for the present molecules, but probably more generally, the claims[8,11] that conventional DF methods strongly overestimate the binding energy should really have been confined just to LSDA variants, and while it is indeed the case that this overestimate is significantly reduced by the [B3LYP] hybrid approach, it is also significantly reduced by any of the present BX methods.

Table 9 gives the errors (as both eV and %) for the copper, silver, and gold diatomics, obtained with L2DZ. What is now clearer is that, with this basis set, while the HF/MP2 errors are all negative, it is only SVWN which has consistently positive errors (except for AgO and AgS) and which thus overestimates the binding energy. The two B3 methods in fact consistently underestimate the dissociation energies, as BPW mainly also

TABLE 9: Errors in Dissociation Energies, LANL2DZ Basis Set

	exptl	exptl	HF		MP2		SVWN		BLYP		BPW		B3LYP		B3PW	
molecule	D_o/eV[a]	D_e/eV[b]	eV	%	eV	%	eV	%	eV	%	eV	%	eV	%	eV	%
CuH	2.73	2.85	−1.51	−53	−0.88	−31	0.48	17	0.04	1	−0.11	−4	−0.13	−5	−0.23	−8
CuO	2.79	2.83	−2.43	−86	−0.83	−29	1.12	40	0.21	7	0.09	3	−0.32	−11	−0.41	−14
CuS	2.80	2.83	−1.66	−59	−0.96	−34	0.62	22	−0.19	−7	−0.14	−5	−0.41	−14	−0.36	−13
Cu_2	2.03	2.05	−1.54	−75	−0.57	−28	0.87	42	0.22	11	0.12	6	−0.04	−2	−0.13	−6
AgH	2.28	2.39	−1.33	−56	−0.81	−34	0.53	22	0.01	0	−0.08	−3	−0.09	−4	−0.16	−7
AgO	2.29	2.32	−3.33	−144	−2.03	−88	−0.66	−28	−1.50	−65	−1.60	−69	−1.82	−78	−1.90	−82
AgS	2.21	*2.23*	−2.55	−114	−2.05	−92	−1.05	−47	−0.31	−14	−0.25	−11	−0.41	−18	−1.74	−78
Ag_2	1.66[c]	1.67	−1.31	−78	−0.49	−29	0.67	40	0.02	1	−0.05	−3	−0.12	−7	−0.18	−11
AgCu	1.765[d]	1.78	−1.34	−75	−0.46	−26	0.85	48	0.19	11	0.11	6	0	0	−0.07	−4
AuH	3.32	3.36	−1.80	−54	−1.15	−34	0.32	10	−0.29	−9	−0.36	−11	−0.41	−12	−0.46	−14
AuO	2.33	*2.36*	−2.99	−127	−1.57	−67	0.71	30	−0.29	−12	−0.37	−16	−0.77	−33	−0.83	−35
AuS	2.59	*2.61*	−2.16	−83	−1.32	−51	0.25	10	−0.65	−25	−0.58	−22	−0.83	−32	−0.77	−30
Au_2	2.30	2.31	−1.59	−69	−0.51	−22	0.52	23	−0.32	−14	−0.28	−12	−0.44	−19	−0.41	−18
AuCu	2.363[d]	2.38	−1.47	−62	−0.44	−18	0.9	38	0.1	4	0.11	5	−0.09	−4	−0.09	−4
AuAg	2.064[d]	*2.08*	−1.37	−66	−0.39	−19	0.75	36	−0.03	−1	−0.02	−1	−0.17	−8	−0.16	−8
	sign		−*ve*		−*ve*		(+*ve*)		±*ve*		(−*ve*)		−*ve*		−*ve*	
RMS, all except AgO			1.86	78	1.01	42	0.73	33	0.26	11	0.24	10	0.39	16	0.61	26[e]

[a] All values from ref 35, except the following: (*c*) ref 9a and (*d*) ref 36a. [b] From $D_e = D_o + hc\omega/2$ using experimental values of ω, except for the four in italics, which use calculated values; any resulting error is less than the uncertaintly in D_o. [e] 16 without AgS.

TABLE 10: Correlation Energies (per Electron; au) Calculated for CuH, CuO, CuS, and Cu_2

method	L2MB	L2DZ	3-21G	6-311G
		Averages		
MP2	−*0.00100*	−0.00974	−0.00823	−0.00926
SVWN	−0.05488	−0.05524	+*0.01824*	+*0.01849*
BLYP	−0.05439	−0.05446	−0.05509	−0.05543
BPW	−0.06102	−0.06106	−0.05796	−0.05804
B3LYP	−0.05698	−0.05699	−0.05386	−0.05397
B3PW	−0.05854	−0.05852	−0.05219	−0.05211
		SD/Avg		
MP2	−*0.74*	−0.07	−0.12	−0.12
SVWN	−0.14	−0.14	+0.12	+0.11
BLYP	−0.05	−0.06	−0.04	−0.04
BPW	−0.05	−0.05	−0.05	−0.05
B3LYP	−0.05	−0.05	−0.04	−0.04
B3PW	−0.05	−0.05	−0.04	−0.04

does, while BLYP is mixed. Thus, the conclusions of the previous paragraph remain the same for this wider group of molecules. [Also apparent is that there is a specific problem with AgO, though just what that problem is is not evident.] The RMS errors in this table include all values except those of AgO. These show that, for these molecules, the hybrid methods are clearly inferior to their pure DFT counterparts, BPW and BLYP.

3.4. Correlation Energies. Whereas the MP2 method, being the "first step up" from HF, can be expected to underestimate the correlation energy, the comment has been made[11] that inadequacies of the current functionals lead to an overestimation of correlation energy for the DFT methods (and that this in turn is what is responsible for the errors in bond lengths and strengths). It is thus of interest to examine the correlation energies of the respective methods. To compare the results from different molecules, calculated from both ECP and all-electron basis sets, it is appropriate to examine the correlation energy per electron included in the calculation (of number n_e), which we take to be given by

$$e^{\mathrm{corr}} = E^{\mathrm{corr}}/n_e = \{E(\mathrm{MP2/DFT}) - E(\mathrm{HF})\}/n_e$$

Table 10 shows the average e^{corr} values of the four copper diatomics for the different methods with both the ECP and the all-electron basis sets, along with the standard deviation divided by the average, which yields an indication of the spread in values between the various molecules (and which, for the BX methods, is very small).

The first thing to note is that the MP2 values are only about one-sixth those of DFT. While a smaller value would be anticipated, it might not be expected that the difference would be this large, perhaps supporting the "DFT overcorrelation" hypothesis. However, the better agreement with experimental results of DFT-calculated properties certainly suggests that any such overcorrelation is proportionally less than the undercorrelation with MP2. Second, it will be observed that the values for BPW are slightly larger than those for the other BX methods. Since BPW does not give worse agreement with experimental results (rather, to the contrary), this further suggests that these DFT methods are indeed not overcorrelated.

The third observation relates to the surprising positive values obtained for SVWN when combined with the all-electron bases. This indicates that SVWN, which allows for both exchange and correlation, is unable to produce as low a total energy as the traditional HF method, which does not include correlation! Apparently, there is some kind of interdependence between the method and the basis set so that the two "simply do not mix". Finally, and somewhat along the same lines, the MP2/L2MB combination yields a particularly small correlation energy and a large variation between molecules, suggesting that this combination, too, is suspect.

3.5. Basis Set Extensions. Having determined the best basis set for the calculations, the most common approach to the further reduction of errors is to augment this by the addition of polarization (higher-*l*) and/or diffuse (higher-*n*/lower-ζ) functions. Whereas the primary choice for first- and second-row elements tends to be the former, for transition/noble metals, it has more commonly been the latter (and particularly, diffuse-*d*).[29]

In addition to this approach to overcome the inherent problem of basis set incompleteness, there is also the problem of basis set superposition error (the increased "function-space" in the molecule, as compared to that in the atom). This effect has been considered by various studies to be a significant source of error in the dissociation energy and attempts to offset this are made by the counterpoise correction (which includes the orbital functions of "ghost" atoms at the molecular positions in the atomic calculation). While the counterpoise method is most commonly encountered in loosely bound "dimer" systems, it

TABLE 11: Analysis of the Effect of Additional Functions to the L2DZ Basis Set in the Calculation of Dissociation Energy

BPW	E_{at}/au	E_{diat}/au	time[a]	$2\Delta E_{at}$/eV[b]	ΔE_{diat}/eV[b]	D_e/eV	% error
Cu_2 (*exptl*)						*2.05*	
L2DZ	−196.2003	−392.4804	1.0	0.000	0.000	2.17	6
L2DZ + 1 × d	−196.2070	−392.4907	1.4	−0.362	−0.282	2.09	2
L2DZ + 2 × d	−196.2117	−392.4967	2.5	−0.619	−0.444	1.99	−3
L2DZ + (2 × s, 3 × p, 2 × d)	−196.2174	−392.5051	4.2	−0.928	−0.672	1.91	−7
Counterpoise(L2DZ)	−196.2046	−392.4804	1.0	−0.233	0.000	1.93	−6
Ag_2 (*exptl*)						*1.67*	
L2DZ	−145.7963	−291.6523	1.0	0.000	0.000	1.62	−3
L2DZ + 1 × d	−145.7996	−291.6571	1.4	−0.178	−0.131	1.58	−6
L2DZ + (1 × s, 1 × p, 1 × d)	−145.7998	−291.6572	2.1	−0.189	−0.133	1.57	−6
Counterpoise(L2DZ)	−145.7979	−291.6523	1.0	−0.087	0.000	1.54	−8
Au_2 (*exptl*)						*2.31*	
L2DZ	−135.4942	−271.0629	1.0	0.000	0.000	2.03	−12
L2DZ + 1 × d	−135.4942	−271.0650	1.5	−0.000	−0.056	2.08	−10
L2DZ + (1 × s, 1 × p, 1 × d)	−135.4958	−271.0669	2.2	−0.092	−0.109	2.05	−12
Counterpoise(L2DZ)	−135.4960	−271.0629	1.0	−0.099	0.000	1.93	−17

[a,b] Values relative to L2DZ.

has also been employed in transition/noble metal-molecules[30a] and recently was found to be necessary to obtain good dissociation energies for nickel and copper diatomics.[30b]

Consequently, further calculations on the dissociation energies of Cu_2, Ag_2, and Au_2 were undertaken to compare the effectiveness of both the addition of diffuse functions and the counterpoise method. Although check calculations were made with the HF method, the errors there are already so large that the corrections are negligible, and so, these refinements are worthless. We therefore report only the results of the BPW method, which we take to be representative of the BX group and complementary to those methods previously employed.[30b] Because of the marked superiority of L2DZ, only this basis set was considered. The orbital exponents of these additional functions are taken from Bauschlicher et al,[31] which in turn incorporates Hay's[29] exponent for the first d function.

Table 11 illustrates the effect on the energies of adding s, p, and d diffuse functions to the basis set and also the calculated value of the counterpoise correction, which estimates the basis set superposition error (BSSE). For the copper diatomic, three results are shown involving the addition of diffuse functions. The first calculation is performed with only Hay's diffuse 3d function, and the second calculation retains Hay's function and adds a further d function. In the third, two s functions, three p functions, and two d functions are added to supplement L2DZ, representative of the 4s, 4p, and 3d orbitals. The columns E_{at} and E_{diat} give the total electronic energies of the atom and the diatomic, respectively. Following the relative calculation time, the next two columns give the changes in these energies, presented so that their difference corresponds to the change in the dissociation energy (relative to the "parent" L2DZ calculation). The final two columns give the dissociation energy itself and its percentage error.

It is observed that the addition of extra functions results in a progressive and significant decrease in the total energy, indicating a significant incompleteness in the original basis set. This does not, however, translate into a corresponding improvement in the dissociation energy.

For copper, the addition of the s, p, and d functions results in no improvement in the calculated D_e and is considerably more expensive in computational time. The calculations involving only d functions, in particular the single diffuse d function, produce more accurate values and so are much more cost-effective. Possibly the reason for this is that the orbital exponent of the single d function was optimized both to the $3d^{10}$ configuration and for a (d-5G) primary basis,[29] as employed by L2DZ, whereas the other exponents are not correspondingly optimized. The counterpoise correction also tends to overcorrect the original L2DZ value and leads to an overreduction in the dissociation energy. This conclusion contrasts with the calculations of Romanowski et al.[30b] on Cu_2, who found that incorporating a similar BSSE into their prediction of the dissociation energy gave better agreement (2.00 vs 2.27 eV) with the experimental value (2.05 eV), due to their initial value being so much larger.

For silver and gold, the diffuse functions consist of first an additional d function and then a calculation using single additional s, p, and d functions. (The exponents are those used by Bauschlicher et al.[32]) In the case of the Ag_2, the addition of diffuse functions gives less accurate results than the original values, while for Au_2, the single diffuse d function performs marginally better. In both cases, the counterpoise correction yields the worst values.

From these results, it appears that, although there is significant basis set incompleteness, there is little or no nett effect in the compensation of basis set deficiencies in using either diffuse functions or the counterpoise correction. If basis set expansion is considered, a single d diffuse function is the best option, although there is only a marginal improvement. The incorporation of the counterpoise correction always leads to a lowering of the dissociation energy, but since the initial value is not always a substantial overestimate, this does not necessarily lead to any improvement—indeed, in no case with the present results. This suggests the possibility that the errors arising from the basis set deficiencies are canceled by compensatory errors in the calculation method so that the overall model is not improved by basis set extensions.

To further investigate this point, we compare in Table 12 the percentage errors for the results in common on CuH, Cu_2, and $CuCH_3$ obtained in the present calculations with those obtained previously[11] using a triple-ζ basis set (plus polarization functions) purposely tailored for copper. Probably the most striking feature is the extremely close similarity between all the results—even down to the two anomalous Cu−C frequencies! While BPW/L2DZ has marginally the lowest RMS error, most of this small difference is due to the method rather than the basis set. More significant in the present context is the virtual tie between B3LYP/L2DZ and B3LYP/TZ2P′. Contrary to what "should" be the case, L2DZ performs just as well for these molecules as its more sophisticated counterpart. This therefore augers well for its application to noble-metal clusters.

3.6. Computational Requirements. It is well-known (eg[6a,33]) that, in terms of the number of basis functions, N, used to represent the molecular orbitals, the notional computational time

TABLE 12: Comparison of Basis Sets

% error	BPW L2DZ (present work)	B3LYP L2DZ (present work)	B3LYP TZ2P′ (ref 11)
r			
CuH	2.0	2.4	0.8
Cu_2	0.9	1.9	2.8
$Cu-CH_3$	2.4	3.2	2.9
D_e			
CuH	−2.7	−3.4	−1.3
Cu_2	6.7	−0.8	−11.0
ν			
CuH	−5.6	−6.1	−3.5
Cu_2	−1.1	−5.3	−1.9
$Cu-CH_3$:s-str[a]	55.9	52.4	52.0
$Cu-CH_3$:d-rck[a]	61.7	63.4	58.0
$(Cu)CH_3$:s-def	−5.8	−3.7	−6.5
$(Cu)CH_3$:d-def	7.0	10.0	8.2
$(Cu)CH_3$:s-str	1.7	3.7	6.9
$(Cu)CH_3$:d-str	7.7	9.7	5.4
RMS (except for *a*)	*4.7*	*5.4*	*5.6*

TABLE 13: Relative CPU Times for Geometry Optimization of $Cu_2(HCO_2)_4$

basis set (# basis fns)/method	L2MB (90)	L2DZ (160)	3-21G (174)	6-311G (246)
HF	1	3	2	9
MP2	4	24	33	*a*
SVWN	1	4	3	5
BLYP	2	5	2	5
BPW	2	5	3	4
B3LYP	1	4	3	6
B3PW	1	4	3	6

[a] Calculation intractable.

for HF increases as N^4, though in practice this reduces to something more like N^2. The time usage further increases when correlation is included, notionally as N^5-N^7 which, even when reduced, imposes a severe constraint on the calculations. The DFT methods, by contrast, are able to include electron correlation with a notional calculation time of N^3, which makes them a promising approach to the investigation of metal−adsorbate interactions. The hybrid methods could be expected to be somewhat less advantageous in this regard.

It is thus of some interest to compare the practical computational efficiencies of the HF/MP2 and DFT methods. It has been observed in our calculations that, while there is not a significant difference in CPU time between the DFT's and MP2 for the diatomics, when larger molecules are involved, in particular those containing more than one metal atom, the density functionals perform much more efficiently. Table 13 contains typical CPU times (relative) for a geometry optimization of a copper-based molecule containing just two copper atoms. It can be seen that the DFT methods present a very substantial saving in computation time compared to MP2. On larger systems, the MP2 calculation time escalated to become unmanageable and, for the copper−phosphine molecule, was completely unsuccessful.

Table 13 also shows how the size of the basis set significantly effects calculation time. As might be anticipated, the double-ζ sets (L2DZ, 3-21G) lie intermediate between the single and triple-ζ. The 3-21G, however, tended to be less reliable than the L2DZ and often experienced technical problems, even with the small-molecule calculations, e.g., Cu_2 and AgCu. This may be because this basis set is not really designed for use in heavy atoms like metals and is simply not flexible enough. For the copper-phosphine molecule, only the LANL2 basis sets were successful (though not for MP2).

The 6-311G basis set, when combined with any of the methods, often greatly tests the available computing resources. Calculations on more complex molecules, which involve both MP2 and a large basis set, such as 6-311G, are often unsuccessful (as for this copper-formate molecule).

Overall, the results confirm the expected trends, with the DFT-based methods showing a major advantage with respect to MP2, and even outperforming HF when the number of basis functions becomes large. What this Table does not reveal, however, is that some of these calculations require “cajoling” in order to make them work, such as running a HF and/or L2MB calculation first. In this regard, the HF-DFT hybrids tend to be more amenable than their pure DFT counterparts. This, indeed, is the only criterion which, for these molecules, favors B3LYP over BPW.

4. Conclusion

Some properties of molecules containing copper, silver, or gold atoms have been calculated using MP2 and a variety of DFT methods, in conjunction with different basis sets. All the density functional methods, including LSDA as well as GGA, show themselves to be generally more accurate and reliable than MP2 in the prediction of geometry, frequencies, and dissociation energies for the “test suite” of molecules for which experimental data are available. They also require much less computation time.

Within either framework accuracy is extremely basis set sensitive. Whereas the LANL2 basis sets (which contain an ECP to approximate the core electrons) are available for all three metals, the 6-311G and 3-21G all-electron basis sets are available only up to Cu and Ag, respectively, so comparisons are somewhat restricted. Nevertheless L2DZ was far superior to the corresponding double-ζ all-electron basis and, for copper, either equaled or outperformed the triple-ζ basis set. Even the minimum basis L2MB produces better results than 3-21G, which furthermore was so unreliable as to make questionable even its continuing availability for these elements.

For the bond lengths, the RMS % errors with L2DZ were SVWN $\approx$ 2, BPW $\approx$ 3, B3PW $\approx$ 3, BLYP $\approx$ 4, B3LYP $\approx$ 4, and MP2 $\approx$ 6. This is consistent with the lore that LSDA yields the best bond lengths. Contrary to some previous results and generalizations, the BX/GGA results were overestimates rather than underestimates, and even for SVWN, the number of underestimates was approximately matched by the number of overestimates. Also in contrast to expectations, the hybrid methods did not yield any improvement over the pure DFTs.

For the vibrational frequencies, the RMS % errors with L2DZ were BPW $\approx$ 6, B3PW $\approx$ 7, BLYP $\approx$ 8, B3LYP $\approx$ 8, SVWN $\approx$ 12, and MP2 $\approx$ 12 (excluding the anomalously large values for the two $Cu-CH_3$ modes). Excluding the same molecule, the actual wavenumbers calculated by the BX methods are underestimated by ~7%, in contrast to the B(3)LYP/6-31G* overestimates of ~2% for organic molecules.[27]

An interesting conclusion from the present results is that, contrary to some expectations, the methods which yield the best frequencies and the best structures are not the same. Indeed, if these respective % errors (for each molecule) are plotted against one another, there is hardly any correlation at all, for any of the methods. Rather than display a collection of fairly meaningless “scatter plots”, Table 14 lists the correlation coefficients of the best-fit straight lines for each method (together with the corresponding line parameters). It can be seen that only for SVWN is there a weak correlation ($R^2 \approx 0.5$), with that of the rest being virtually zero ($R^2 < 0.1$).

TABLE 14: (Non)Correlation between Frequency and Bond Length Errors. $\xi_\omega = m\xi_r + b$ with Correlation Coefficient R^2

method	HF	MP2	SVWN	BLYP	BPW	B3LYP	B3PW
m	−1.12	−0.27	−2.46	−0.51	−0.39	−0.24	−0.16
b	−6.57	−8.20	+7.37	−5.13	−3.86	−6.43	−5.55
R^2	0.170	0.007	0.527	0.082	0.064	0.018	0.010

For the dissociation energies, the RMS % errors with L2DZ were BPW ≈ 7, BLYP ≈ 8, B3LYP ≈ 10, B3PW ≈ 11, SVWN ≈ 30, and MP2 ≈ 30 (excluding the anomalously large values for AgO). As expected, the MP2 and SVWN energies were under- and overestimates, respectively. What was not anticipated was that the B3 results were all underestimates. While this might be viewed as an "over-replacement" of DF by HF exchange, the fact that most of the BPW values were also underestimates precludes such a simple interpretation. While the addition of diffuse functions to the L2DZ basis set lowered the total energies for both the metal atoms and the diatomic molecules (so indicating basis set incompleteness), this was not accompanied by corresponding improvements in the dissociation energies. The same also held for the counterpoise correction. This reinforces the point that it is the method/basis set combination (the "model chemistry") that is important, rather than either component individually. Now, unlike configuration-interaction methods, which have a well-defined theoretical path, DFT methods contain a degree of empiricism in their form and parametrization, which is not necessarily basis set agnostic. Hence, while the former might be expected to benefit from a more complete basis set, the same need not necessarily be true of the latter. The way to ascertain this is, as in the present study, by comparing the respective model chemistries.

The correlation energies were close to 1.5 eV per electron (with ∼10% variation) for all the BX methods with all basis sets. Despite this value being ∼6× larger than that of MP2, since the greatest values were obtained with the method which also produced the best results (BPW), this does not suggest that the DFT methods are overcorrelated. The values with the two L2MB/L2DZ and 3-21G/6-311G pairs were almost identical with the BX methods and also quite similar to one another. With SVWN, however, whereas the LANL2 values were similar to those of the BX methods, the all-electron values were actually of opposite sign (anticorrelation!), suggesting a method/basis set incompatibility.

Overall, while the results of the present investigation reinforce those of several previous studies in relation to the superiority of the DFT methods collectively (an in particular, GGA) over MP2, there is no consistency on the relative virtues of the individual DFT variants. Thus, the conclusions from studies on a smaller set of copper-containing molecules were that B3LYP was to be preferred over BLYP (and BP86);[11] on transition metal hydrides, that B3LYP was slightly superior to both B3PW91[10a] and BLYP;[10b] on cuprous-ion amines and other nitrogen-containing ligands, that B3PW91 was possibly better than B3LYP[12] (though referenced to G2-calculated values, not experiment); and on the single CrC molecule, that B3LYP was better than BPW91[34] (though referenced to multiconfiguration CI, not to experiment). While the present investigation is the most wide ranging, both in terms of systems studied and methods employed, this does not mean that the superiority found for BPW91 with LANL2DZ will necessarily extend to all other transition-metal-containing molecules.

It is nevertheless encouraging that the DFT methods could successfully be used to produce reasonably accurate results in computations involving a significant number of heavy metal atoms, although further work to build a more extensive library of results would be beneficial. The superiority of BPW91 contrasts with the results for organic molecules, where the hybrid B3LYP method has been recommended.[23c] The combination BPW/L2DZ produced low average errors in bond lengths and angles, vibrational frequencies and dissociation energies. This "model chemistry" is thought to provide the most accurate and tractable approach for extension to clusters of noble-metal atoms.

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