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Relativistic treatment of excited electronic states of atomic copper

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Summary. The ^2S_g ($d^{10}s^1$), ^2D_g (d^9s^2), ^2P_u ($d^{10}p^1$), $^{2,4}\{F, P\}_u$ ($d^9s^1p^1$) states of copper as well as the ^1S_g (d^{10}) state of the positive copper ion are studied by *ab initio* methods. Relativistic wavefunctions are determined variationally solving a one-component no-pair equation. This approximation makes it possible to treat all the states in a common set of orbitals. It is found that differential relativistic effects for the excitation energies are independent of the one-particle basis employed. The first-order perturbation estimate using the mass-velocity and Darwin operators depends critically on the description of the $3s$ and $3p$ core electrons. Among the various one-particle sets tested, ^2D_g orbitals, with the ($4s$, $4p$) near-degeneracy effects included in the orbital optimization step, are most appropriate for the correlation treatment. They give an error of 0.3 eV for the ^2S_g–^2D_g separation only slightly inferior to our best result employing parent orbitals for both states. All other states agree with experiment to within 0.2 eV. The first-order spin-orbit splitting of the ^2D_g state ($-2006\,\mathrm{cm}^{-1}$) is in excellent agreement with the experimental value.

Key words: Copper – Excited electronic states – Relativistic wavefunctions

1. Introduction

Several electronic states are known to be involved in reactions of atomic copper with other atomic or molecular species. In its atomic $3d^{10}4s^1$ ground state, copper is ideally suited for binding to a single monovalent ligand such as hydrogen or the halogen atoms. These CuX compounds have more or less ionic $^1\Sigma^+$ ground states with predominately d^{10} character [1–3]. The first excited states of CuH, on the other hand, are best described by the interaction of hydrogen with copper in a $3d^94s^14p^1$ configuration [4]. States with d^9 character are also involved if a bond to a bivalent species like oxygen or sulfur is formed [5]. In side-on reactions with diatomic molecules like H_2 and O_2, where two bonds have

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to be formed simultaneously, the ^2P_u ($3d^{10}4p^1$) has been shown to be especially active in the initial process [6–9] followed by an avoided crossing to a potential surface correlating with the ^2D_g ($3d^94s^2$) state of copper. One prerequisite for a correct computational description of the aforementioned reactions is to obtain the atomic energy splittings with sufficient accuracy. For states with different d occupations this is very difficult due to the large amount of correlation energy contained in the $3d$ shell. Considerable errors are found for the ^2D_g–^2S_g separations at the single reference correlated level [10–13].

Focusing on properties of molecular ground states and perhaps a few of the low-lying excited states in transition metal compounds, multi-configurational self-consistent field (MCSCF) orbital optimizations for each state followed by a multi-reference configuration interaction (MRCI) or an averaged coupled pair functional (ACPF) treatment have proven to give very reliable results [14–16]. If, however, transition moments and off-diagonal coupling matrix elements are required, the use of a common one-particle basis is mandatory. One of the goals of the present work is to find a common one-particle basis which allows one to describe the aforementioned electronic states of neutral and ionic copper in subsequent electron correlation treatments without significant loss of accuracy.

At the end of each transition metal row relativistic effects play an important role [17]. An easy and cheap way to account for relativistic effects in all-electron calculations is the use of the mass-velocity and Darwin (MVD) operators [18] in first-order perturbation theory. For the first and second transition-metal row, this approach was shown [17, 19] to give atomic energy separations in satisfactory agreement with Dirac–Fock splittings. In the past, it has been successfully applied to estimate the relativistic changes of binding energies, equilibrium distances, excitation energies etc. in a large variety of molecular systems. Problems with this approach do occur, however, if a correlation calculation on a specific state is performed in an orbital basis of another state or if frozen core orbitals are employed in the orbital optimization step. On the basis of a double perturbation theory formalism, Schwarz et al. [20] noted that there might be significant relativistic contributions to electronic excitation energies due to the core orbitals. In frozen core calculations on various states of atomic palladium, Blomberg and Wahlgren [21] found that the relativistic correction was severely underestimated in a first-order treatment. They also showed at the SCF level that the error is decreased to a large extent when a no-pair operator (in this case with free-particle projection) is employed variationally. In this work we will use a more advanced no-pair theory containing projectors to the solutions for an electron in an external Coulomb field [22–25]. The question arises whether it will be possible to obtain relativistic corrections in a basis of common orbitals comparable to those found when each state is calculated in its own set of orbitals.

2. Computational details

2.1. *Methods*

Relativistic effects are accounted for in the calculations by solving a one-component spin-free approximation to the no-pair equation. Alternatively, for test purposes the well-known mass-velocity and Darwin (MVD) operators [18] have been used in first-order perturbation theory. The no-pair operator employed variationally in this work contains external field projectors for the one-particle terms while the electron-electron interaction is described by the unmodified Coulomb operator. The theoretical background of the no-pair equations [22–25] and the approximations made in its implementation in electronic structure code [26, 27] have been discussed in detail elsewhere. The momentum-dependent operators, which occur in the formalism, are evaluated in the basis of linear combinations of fourier-transformed gaussians which diagonalize $p^2/2m$. To improve the description of momentum space, contracted basis sets of gaussian functions are resolved into primitives in this step.

The one-particle bases for the ^2S_g or ^2D_g states of copper are determined either by the SCF, MCSCF [28], or natural orbital (NO) procedures. The choice of the configuration spaces for the MCSCF calculations is discussed in detail in Sect. 2.2.

A variety of methods was employed to account for electron correlation. Single-reference calculations in the basis of parent SCF orbitals were performed using the direct singles and doubles configuration interaction (SDCI) procedure [29] or the size consistent (modified) coupled pair functional (CPF) [30] and MCPF [31] methods. Two multi-reference SDCI approaches have been applied in this work: the direct externally contracted CI (CCI) [32] and the conventional MRD-CI [33] with energy extrapolation. Both methods make use of second-order perturbation theory to estimate coefficients or energy contributions of configuration state functions (CSFs) not included in the variation process.

Spin-orbit coupling matrix elements were evaluated for MRD-CI wavefunctions [34] in first-order perturbation theory employing the one- and two-particle Breit–Pauli operators [35].

2.2 Details of the calculation

All AO basis sets employed in this work include the $14s9p5d$ (^2S_g) primitive set of Wachters [36], augmented by the diffuse d function given by Hay [37]. In basis A as s function with exponent 0.33 [38], two p polarization functions [36] with scaling factor $\sqrt{1.5}$ and three contracted f functions [38] were added. The totally symmetric component of the d- and the p-type combinations of the f functions are discarded. The contraction coefficients were determined in atomic nonrelativistic or no-pair SCF calculations on $(d^{10}s^1)$ ^2S_g, respectively. In the nonrelativistic calculations a 6111111111/3311111/3111/211 contraction scheme was applied. Because of the large difference of the $3p$ orbital expansion in the (d^9) and (d^{10}) states, in the no-pair treatment the contraction was changed to 6111111111/5111111/3111/211.

The most diffuse p functions in AO basis A are used to both describe the polarization of the $4s$ orbitals and the $4p$ orbitals in the excited atomic states. Optimal exponents for these states were determined at the nonrelativistic CI level. The smallest p exponent contained in the AO bases described above (0.069299), is only slightly larger than the optimal $4p$ exponent (0.056) for the $(d^{10}p^1)$ occupation; the p orbitals of the different space and spin couplings of the $(d^9s^1p^1)$ configuration have very similar exponents, with a mean value of 0.089. Basis B contains these two optimized $4p$ functions in addition to the $14s9p6d$ set and two primitive f functions with exponents 2.89 and 0.4. As the largest relativistic effects emerge from the s shells, for test purposes only the p and d sets were contracted, yielding a $[14s, 6p, 4d, 2f]$ set. In this case all cartesian components of the d and f functions were retained.

The single-reference calculations were performed in the basis of SCF orbitals of the respective state. The first of the MCSCF configuration spaces is of complete active space (CAS)-type. In case of the ^2D_g state it consists of all configurations of proper space- and spin-symmetry that can be generated by distributing two electrons in the $4s$ and $4p$ orbitals and is denoted as CAS(s, p). This level of treatment corresponds to an SCF calculation for the ^2S_g state. The second type of active spaces comprises the $4s$, the $3d$ and $3d'$ orbitals but in this case the configurations space was restricted to CSF's containing a fixed number of electrons in σ, π, and δ subspaces. This active space will be designated as CAS11 and is used for the ^2S_g calculation. Addition of the important $s^2 \rightarrow p^2$ excitations for ^2D_g is beyond the capacities of our present version of the CASSCF program [28]. Instead, we take the s and d orbitals from the CAS(d, d') and the p and f orbitals from CAS(s, p) calculations. This type of orbitals, which has already been successfully employed for the negative copper ion [39], is denoted as CAS*mix*.

In cases in which the configuration space for a CI expansion of an electronic state is spanned by one-particle functions that have been optimized for that particular state (parent orbital calculations), CI reference configurations can be selected according to their weights in the underlying MCSCF calculation. All CSF's with coefficients larger than 0.02 in the corresponding (MC)SCF expansions were included in the CI reference spaces. If a common set of orbitals is employed for all states other criteria for choosing the reference sets must be devised. In this case, the reference sets for the MRD-CI calculations using AO basis B consisted of the respective SCF configuration, augmented by $s \rightarrow s'$, $p \rightarrow p'$, and $d \rightarrow d''$ single excitations to account for relaxation. For the ^2D_g state also the important $s^2 \rightarrow p^2$ excitations were included. Slightly larger reference sets, describing valence-orbital relaxation also by virtual orbitals with higher Fock energies, were employed using AO basis C. Regarding the $d^9s^1p^1$ occupation several cartesian components exist in each of the irreducible representations of the D_{2h} subgroup with *ungerade* symmetry. In this case all the components that transform according to a specific irreducible representation of D_{2h} are given as reference configurations, augmented by $s \rightarrow s'$, $p \rightarrow p'$, and $d \rightarrow d''$ single excitations. Maintaining symmetry in the generated CI space for the $d^9s^1p^1$ state requires to include configurations in the reference set with symmetries other than that of the desired CI wavefunction. For technical reasons, this is not possible in the present version of the MRD-CI program [33]. These restrictions in the reference space cause angular symmetry breaking and lead to small, but non-negligible interaction matrix elements between P_u, D_u, and F_u states.

The threshold for configuration selection in the MRD-CI procedure was set to $5 \times 10^{-6}\, E_H$ if not stated otherwise. Single excitations from the leading reference configuration are always included, irrespective of their energy contribution.

3. Results and discussion

3.1. SCF *calculations*

We have checked the accuracy of our relativistic approach by comparing orbital energies and radial expectation values obtained from no-pair SCF calculations with numerical Dirac–Fock (DF) values [40]. The orbital energies calculated for the ^2S_g state in the uncontracted $15s11p6d$ AO basis and the corresponding DF orbital energies are given in Table 1. Excellent agreement between the two sets of data is observed. The largest deviation occurs for the $3d$ orbital (0.35%) and is probably due to AO basis set deficiencies. A more detailed analysis is possible for the radial expectation values $\langle r^{-2} \rangle$, $\langle r \rangle$, and $\langle r^2 \rangle$, which probe the orbital shapes in different spatial regions. It should be noted, however, that the expectation values calculated from wavefunctions expressed in a basis of two-component spinors are not directly comparable to expectation values obtained in the four-component (Minkowski) representation but rather require transformation of the corresponding operators by means of a Douglas–Kroll transformation [23], analogous to transformation of operators in Foldy–Wouthuysen theory [35]. The expectation values obtained from a nonrelativistic LCAO-SCF calculation (Table 2) are found to be in very good agreement with the numerical Hartree–Fock values by Desclaux [40]. This is also true for the relativistically calculated expectation values $\langle r \rangle$ and $\langle r^2 \rangle$ which have their largest weights in the outer orbital region and describe the bonding characteristics. $\langle r^{-2} \rangle$, which emphasizes the inner orbital region, is in satisfactory agreement with the DF values for the p and d shells, while all the s orbitals are somewhat too compact in this regime. The difference arises probably from the different treatments of the nucleus. In DF theory [40], the nucleus is assumed to be finite as opposed to a pointlike nucleus in the current no-pair equations.

The radial extents of the $(3d^9 4s^2)$ ^2D_g SCF orbitals, also displayed in Table 2, show remarkable differences to those of $(3d^{10}4s^1)$ ^2S_g. As expected, the d shell is more compact for the d^9 occupation than for d^{10}. As a consequence of the presence of the d hole, also the $3s$ and $3p$ shells in the ^2D_g state are slightly more contracted than the corresponding ^2S_g orbitals. Since the $4s$ orbital is doubly-occupied in the ^2D_g state, one would generally expect it to be more diffuse than the singly-occupied $4s$ orbital in the ^2S_g state. The less complete nuclear shielding by the d^9 shell prevails, however, and leads to a considerably more dense electron distribution in the $4s$ orbital.

As the energy changes due to the kinematic relativistic effects are largest for the innermost electrons it is not clear from the beginning whether the usual AO basis set contraction procedure will work in case of no-pair calculations. As already mentioned, in the integral evaluation step the contraction has to be resolved to improve the matrix representation of the momentum operator.

Table 1. SCF orbital energies $[E_H]$ for the $(d^{10}s^1)$ ^2S_g and (d^9s^2) ^2D_g states of copper obtained in basis A

Orbital	^2S_g, DF [40]	^2S_g, no-pair this work	^2D_g, no-pair this work
$1s$	-332.6545	-332.46756	-332.70062
$2s$	-41.67184	-41.66517	-41.92294
$3s$	-5.15650	-5.15849	-5.40148
$4s$	-0.24477	-0.24455	-0.29083
$2p$	-35.81072[a]	-35.81157	-36.06470
$3p$	-3.36288[a]	-3.36661	-3.59255
$3d$	-0.47973[a]	-0.47805	-0.71979

[a] weighted averaged over $j = l + 1/2$ and $l - 1/2$ components

Table 2. Radial expectation values of atomic SCF orbitals for $(d^{10}s^1)$ ^2S_g and (d^9s^2) ^2D_g (AO basis *B*)

	^2S_g, numerical HF [40]		^2S_g, this work		^2D_g, this work	
			$\langle r^{-2}\rangle[a_0^{-2}]$			
Orbital	relat.	nonrel	relat.	nonrel	relat.	nonrel
1*s*	1750.0	1635.5	1897.1	1634.0	1897.1	1634.0
2*s*	173.96	158.29	188.74	158.27	188.73	158.26
3*s*	25.405	23.054	27.503	23.069	27.797	23.329
4*s*	0.9131	0.8081	0.9852	0.8151	1.3193	1.1059
2*p*	53.497[a]	51.788	53.084	51.804	53.076	51.796
3*p*	7.4248[a]	7.1668	7.3999	7.1887	7.4902	7.2801
3*d*	2.6861[a]	2.7023	2.6711	2.6872	2.8681	2.8845
			$\langle r\rangle[a_0]$			
Orbital	relat.	nonrel	relat.	nonrel	relat.	nonrel
1*s*	0.0521	0.0529	0.0518	0.0529	0.0518	0.0529
2*s*	0.2339	0.2375	0.2339	0.2375	0.2339	0.2375
3*s*	0.7128	0.7228	0.7130	0.7227	0.7090	0.7184
4*s*	3.2615	3.3311	3.2511	3.3141	2.9249	2.9678
2*p*	0.2061[a]	0.2075	0.2058	0.2075	0.2058	0.2075
3*p*	0.7530[a]	0.7577	0.7522	0.7573	0.7460	0.7509
3*d*	0.9976[a]	0.9912	0.9975	0.9915	0.9258	0.9206
			$\langle r^2\rangle[a_0^2]$			
Orbital	relat.	nonrel	relat.	nonrel	relat.	nonrel
1*s*	0.0037	0.0037	0.0036	0.0037	0.0036	0.0037
2*s*	0.0646	0.0665	0.0646	0.0665	0.0646	0.0665
3*s*	0.5872	0.6035	0.5876	0.6034	0.5801	0.5954
4*s*	12.552	13.084	12.443	12.907	10.061	10.354
2*p*	0.0521[a]	0.0528	0.0520	0.0527	0.0520	0.0527
3*p*	0.6704[a]	0.6783	0.6692	0.6780	0.6567	0.6648
3*d*	1.3556[a]	1.3351	1.3457	1.3272	1.1250	1.1103

[a] weighted average over $j = l + 1/2$ and $l - 1/2$ components

Employing the no-pair operator in the uncontracted 15*s*11*p*6*d* basis, ^2D_g is located 0.07 eV below ^2S_g at the SCF level, close to the numerical relativistic (Cowan–Griffin) Hartree–Fock results of Martin et al. (0.06 eV) [19]. Contracting this basis to [9*s*7*p*4*d*] functions has almost no effect on the excitation energy. The contraction error in the relativistic calculation is 0.02 eV, comparable to the nonrelativistic case for which an error of 0.01 eV was found. If no equivalence restrictions are imposed the symmetry in the ^2D_g wavefunction is broken and the energy of this state is lowered. This error should, however, be remedied in the subsequent electron correlation treatments. Due to this symmetry breaking, both in relativistic and nonrelativistic calculations the energy of ^2D_g is lowered by 0.04 eV in the 15*s*11*p*6*d* basis and by 0.07 eV if the *f* functions are added. The no-pair SCF excitation energy in the contracted [9*s*7*p*4*d*3*f*] basis set, finally, amounts to -0.12 eV not imposing equivalence restrictions.

3.2. Parent orbital calculations

In this section we discuss the influence of various electron correlation treatments on the ^2S_g–^2D_g splitting at the nonrelativistic level. Throughout the respective parent orbitals are employed. For being able to compare our results with experiment, we have added the no-pair correction (0.43 eV) to the J-averaged experimental energy separation of 1.49 eV [41]. The nonrelativistic experimental reference amounts then to 1.92 eV.

The calculated excitation energies of the ^2D_g atomic state are compiled in Table 3. Let us first concentrate on the single-reference calculations in which only 11 valence electrons are correlated. The ^2S_g–^2D_g splitting is found to be nearly independent of the electron correlation approach. The energy separations resulting from the coupled pair functional methods (CPF and MCPF) are slightly smaller than the SDCI values while the estimate of higher excitation contributions by means of the Davidson formula [42] has almost no differential

Table 3. Summary of the nonrelativistic $^2S_g - {}^2D_g$ excitation energies [eV] using AO basis A

Method	Orbitals	$^2S_g - {}^2D_g$
single-reference calculations		
SDCI	SCF	1.56
SDCI + DC[a]		1.55
MRD-CI(1)		1.53
MRD-CI(1) + DC[a]		1.50
CCI		1.36
CCI + DC[a]		1.34
CPF		1.50
MCPF		1.51
MCPF(3*s*, 3*p* CV[b])		1.54
MCPF(3*s*, 3*p*)		1.48
MCPF	frozen core SCF[c]	1.57
multi-reference calculations		
MRD-CI	SCF	1.39
MRD-CI + DC[a]		1.51
MRD-CI	SCF/CAS(*s*, *p*)[d]	1.27
MRD-CI + DC[a]		1.44
MRD-CI	CAS11/CAS*mix*[d]	1.56
MRD-CI + DC[a]		1.55
MRD-CI	INO1	1.63
MRD-CI + DC[a]		1.63
MRD-CI	INO2	1.65
MRD-CI + DC[a]		1.65
nonrelativistic experimental reference[e]		1.92

[a] including Davidson correction or its multireference analog
[b] configurations contain at most 1 hole in the 3*s* and 3*p* shells
[c] argon core frozen from an SCF calculation on the average of ^2S_g and ^2D_g
[d] orbital designation see Sect. 2.2
[e] weighted average over fine-structure levels 1.49 eV [41] with a relativistic correction of 0.43 eV added

effect. The extrapolated energies for the truncated single-reference calculations, denoted as MRD-CI(1) in Table 3, differ only slightly from the corresponding SDCI results. Because of the somewhat lower correlation energies and the higher weight of the reference configurations in the truncated CI expansions, the Davidson correction to the MRD-CI energy is underestimated. At this level, the MRD-CI(1) result deviates from the Davidson corrected SDCI value by 0.05 eV. Larger deviations, especially for the ground state energy, are found for the externally contracted CI (CCI) approach. In this method, the relative CI expansion coefficients are kept fixed for all CSF's with a common structure in the internal space [32]. The large error arises from the extraordinarily small number of free variational parameters in this case (73 for ${}^2S_g$). In calculations, in which the number of internal walks and free parameters is larger, the approximations are less aggravating [14]. Disregarding the CCI results, the nonrelativistic excitation energies range from 1.50 to 1.56 eV. Similar to the situation for the d^8–d^9 and d^9–d^{10} splittings in atomic nickel only a slight improvement on the ${}^2S_g-{}^2D_g$ energy separation with an AO basis set saturation is observed at the SDCI level. Using a $[7s6p4d2f1g]$ ANO basis, Partridge [43] obtained an SDCI value of 1.62 eV compared to 1.56 eV in AO basis A. The effect of further enlarging the AO basis at this level of correlation treatment is probably rather small.

In the ${}^2D_g$ state, the $3d$ shell is spatially closer to the $3s$ and $3p$ shells as compared to the ${}^2S_g$ orbitals. Thus, for this state, a larger $\{3s, 3p\}-3d$ correlation per d electron results. In the ${}^2S_g$ state, on the other hand, the number of $\{3s, 3p\}-3d$ electron pairs is larger. The change of the ${}^2S_g-{}^2D_g$ separation due to inclusion of the $3s$ and $3p$ core electrons in the correlation treatment was found to be negligible in previous SDCI calculations on copper [11]. The results of Sunil and Jordan [12], on the other hand, indicate a stabilizing effect of $3p-3d$ correlation of 0.8 eV on ${}^2D_g$ when two f functions (exponents 1.8 and 0.5) are present in the AO basis. In absence of these polarization functions, a large differential effect (0.24 eV) in the opposite direction was observed. Since 19 electrons have to be correlated, the size-consistent MCPF approach should be more appropriate than SDCI treatments. The present MCPF calculations confirm the small differential effect of $\{3s, 3p\}$ correlation. In this approximation, core-valence correlation increases the ${}^2D_g$ excitation energy by 0.03 eV. Inclusion of core-core correlation, on the other hand, stabilizes the d^9 state yielding a net effect of -0.03 eV on the ${}^2D_g-{}^2S_g$ separation. Thus, to a good approximation it should be possible to neglect $\{3s, 3p\}$ correlation for valence excitations in copper.

The large discrepancy of the ${}^2D_g$ excitation energy at the single reference correlated level with experiment is very disappointing. The disagreement becomes even worse if the $(4s, 4p)$ near-degeneracy is accounted for in the description of ${}^2D_g$. If the $4s^2 \rightarrow 4p^2$ excitations are included in the CAS and CI reference spaces, the deviation from experiment is raised to 0.48 eV at the Davidson corrected level. Similar discrepancies were obtained in the past for the ${}^3F_g(d^8s^2)$, ${}^3D_g(d^9s^1)$ and ${}^1S_g(d^{10})$ energies of the neighboring nickel atom [44–46]. Inclusion of radial $3d \rightarrow 3d'$ correlation already in the orbital optimization step reduced the error for the ${}^3D_g-{}^1S_g$ excitation to 0.14 eV [44]. The calculated ${}^3F_g-{}^3D_g$ separation is, however, still off by 0.27 eV after Davidson correction [44]. In copper, $3d \rightarrow 3d'$ correlation tends to favor the d-rich ${}^2S_g$ state. We have optimized $3d'$ orbitals in CASSCF calculations (CAS11/CAS*mix*) and include all important $3d^2 \rightarrow 3d'^2$ in the reference spaces of the subsequent multi-reference CI treatments. While we use the same type of CAS expansion as Bauschlicher et al. on the atomic states of nickel [44], we employ the conventional MRD-CI procedure instead of a direct multi-reference complete singles doubles CI as applied by these authors. The CSF selection threshold was lowered to $5 \times 10^{-8}\,E_H$ in this case. Starting with the CAS11/CAS*mix* orbitals, a nonrelativistic excitation energy of 1.56 eV is obtained. The differential effect of the Davidson correction amounts to merely 0.01 eV. Also, on an absolute scale it is much smaller than for the CI calculations employing a small reference space because many quadruple excitations to the leading reference are already included in the CI expansion. Since we could not afford a full second-order CI, attempts were undertaken to increase the percentage of the included correlation energy by performing several natural orbital (NO) iterations. No further references became important during the iteration process. One drawback of the INO procedure is that the total energy is not continuously improved. The total energies for both states increased in the third NO iteration and therefore the iteration process was terminated here. After two NO iterations, the ${}^2S_g-{}^2D_g$ separation has raised to 1.65 eV which is in error by 0.27 eV compared to the nonrelativistic experimental reference. The energy gain in the ${}^2S_g-{}^2D_g$ splitting during the NO iteration process points to the significance of higher-order terms for the differential correlation energy. The importance of these higher-order contributions will be even more pronounced in AO bases containing larger sets of polarization functions.

3.3. *Common orbital calculations*

In order to find a common set of orbitals which is suited for describing electronic states with different d occupations, we have studied various states of neutral and ionic copper: Cu: ${}^2S_g$ $(d^{10}s^1)$, ${}^2D_g$ (d^9s^2), ${}^2P_u$ $(d^{10}p^1)$, ${}^{2,4}\{F, P\}_u$ $(d^9s^1p^1)$ and Cu$^+$: ${}^1S_g$ (d^{10}). Several one-particle bases were tested in this series: ${}^2S_g$ SCF orbitals, ${}^2D_g$ SCF orbitals, ${}^2D_g$ CAS(s, p) orbitals, ${}^2S_g-{}^2D_g$ averaged SCF orbitals, and ${}^2S_g-{}^2D_g$ averaged NOs. We shall discuss here only the results of the nonrelativistic calculations and postpone the discussion of the relativistic effects to the next section. Total energies for the $(d^{10}s^1)$ ${}^2S_g$ ground state and excitation energies for the higher-lying electronic states are given in Table 4.

In this series, the lowest total energies for all states are obtained in the basis of ${}^2D_g$ (d^9s^2) orbitals. While expected for the d^9 states, this is very surprising for the states with d^{10} occupation. On an absolute scale, the total energy of the ${}^2S_g$ ground state in the basis of ${}^2D_g$ orbitals is lowered by as much as 0.33 eV as compared to the CI energy in the basis of ${}^2S_g$ SCF orbitals. For the d^9 states, the dependence on the choice of one-particle set is even more pronounced. As seen from Table 4, the excitation energies of the d^9 states differ by up to 0.45 eV for the ${}^2S_g$ and ${}^2D_g$ based calculations. If near-degeneracy effects between the 4s and 4p shells are included in the orbital optimization step (${}^2D_g$ CAS(s, p)), the weight of the $s^2 \rightarrow p^2$ excitations in the ${}^2D_g$ CI expansion increases considerably. At the CI level, the excitation energy of this state drops by 0.15 eV. Accounting for higher than double excitations by means of the Davidson correction has a compensating effect; but still an energy gain of 0.09 eV relative to the ${}^2D_g$ SCF based results is observed. The other states are affected only little by this procedure as seen from a comparison of their energies in the ${}^2D_g$ SCF and CAS(s, p) bases in Table 4.

Table 4. Summary of nonrelativistic excitation energies obtained at the MRD-CI level. Energies including a multireference analog of the Davidson correction are given in parentheses

		One-Particle Basis (AO basis *A*)				One-Particle Basis (AO basis *B*)		
	State	^2S_g SCF	^2D_g SCF	^2D_g CAS(s, p)	aver. SCF	^2S_g SCF	^2D_g SCF	aver. NOs[a]
Cu	^2S_g $(d^{10}s^1)$	.22653[b] (.24806)[b]	.23871[b] (.25551)[b]	.23783[b] (.25467)[b]	.23139[b] (.25557)[b]	.26528[b] (.28399)[b]	.27397[b] (.28883)[b]	.26617[b] (.28406)[b]
Cu	^2D_g (d^9s^2)	1.64 (1.87)	1.72 (1.71)	1.57 (1.62)	1.68 (1.89)	1.64 (1.81)	1.57 (1.57)	1.78 (1.81)
Cu	^2P_u $(d^{10}p^1)$	3.82 (3.88)	3.94 (3.96)	3.98 (3.97)	3.83 (3.93)	3.69 (3.74)	3.85 (3.74)	3.81 (3.76)
Cu	^4P_u $(d^9s^1p^1)$	5.36 (5.45)	4.95 (4.99)	4.90 (4.93)	5.09 (5.30)	5.34 (5.39)	4.94 (5.04)	5.32 (5.34)
Cu	^4F_u $(d^9s^1p^1)$	5.44 (5.55)	5.18 (5.26)	5.13 (5.19)	5.18 (5.38)	5.56 (5.62)	5.18 (5.29)	5.42 (5.42)
Cu	^2F_u $(d^9s^1p^1)$	5.77 (5.89)	5.63 (5.71)	5.55 (5.60)	5.49 (5.67)		5.53 (5.63)	5.57 (5.52)
Cu	^2P_u $(d^9s^1p^1)$	5.86 (5.96)	5.64 (5.71)	5.65 (5.70)	5.72 (5.91)			
Cu$^+$	^1S_g $(d^{10}s^0)$	7.14 (7.27)	7.22 (7.31)	7.22 (7.30)	7.20 (7.34)	7.25 (7.37)	7.21 (7.30)	7.27 (7.37)

[a] averaged natural orbitals from an MRD-CI treatment of ^2S_g and ^2D_g in the basis of ^2S_g SCF orbitals

[b] total energies; the energy offset is $-1639\ E_H$

Two types of averaged orbitals were tested: SCF orbitals optimized for an equal weight of ${}^2S_g$ and ${}^2D_g$ exhibiting a net d population of 9.5, and averaged natural orbitals from an MRD-CI treatment of ${}^2S_g$ and ${}^2D_g$. The results obtained in the averaged SCF orbital basis look very reasonable. Total energies and energy separations lie in between the values employing ${}^2S_g$ and ${}^2D_g$ orbitals, respectively. The NOs, on the other hand, are clearly biased towards ${}^2S_g$; absolute and relative CI energies in the NO one-particle set resemble closely those of the ${}^2S_g$ orbital-based treatment. This is easily understood from the fact that the underlying CI calculations for generating the NOs were performed in a common basis of ${}^2S_g$ SCF orbitals. A single NO iteration is not capable of overcoming the orbital bias towards ${}^2S_g$.

To elucidate the origin of the high sensitivity of the MRD-CI energies with respect to the choice of one-particle bases, expectation values of the truncated CI expansions for several CSF selection thresholds T and extrapolated MRD-CI energies are compared in Table 5. At $T = \Delta T = 5 \times 10^{-6}\, E_H$, the variationally determined energy of ${}^2S_g$ is lower in the basis of its own SCF orbitals than the corresponding value employing ${}^2D_g$ SCF orbitals; for this CI space of selected configurations it is the (estimated) contribution of the discarded CSF's that reverses the energetical ordering. At the smaller threshold ($T = \Delta T = 5 \times 10^{-7}\, E_H$), many of the formerly discarded CSF's have been directly included in the CI space and both variational and extrapolated CI energies are lower in the basis of ${}^2D_g$ orbitals. While the CI eigenvalues change, of course, drastically with the selection threshold, the extrapolated energies remain fairly stable. We are thus quite confident that the effect that the CI energies obtained in the ${}^2D_g$ one-particle basis are lower than those in the ${}^2S_g$ basis is not caused artificially by the extrapolation procedure but results from the slow convergence of the CI expansion in the basis of the rather diffuse ${}^2S_g$ SCF orbitals. Next, we would like to discuss possible sources of errors which could be responsible for the energy loss observed for the d^9 states in the basis of ${}^2S_g$ SCF orbitals. All important single excitations of the leading configurations are included in the reference set. Thus, the energy increase is not due to a simple orbital relaxation problem. Also, as may be seen from Table 3, there is almost no

Table 5. Nonrelativistic MRD-CI energies $[E_H]$ of the ${}^2S_g$ and ${}^2D_g$ states as a function of the CSF selection threshold T (AO basis A)

State	$T\,[E_H]$	sel. CSF's[a]	$\sum c_{ref}^2$	$E_{CI}(T)$	$E_{CI}(T + \Delta T)$	$E_{extr.}$	$E_{extr.} + Dav$[b]
${}^2S_g$ SCF orbitals (energy offset $-1639\, E_H$)							
${}^2S_g$	5×10^{-6}	5371	0.947	.219360	.212466	.226530	.248064
${}^2S_g$	5×10^{-7}	9333	0.946	.226209	.225552	.227082	.249020
${}^2D_g$	5×10^{-6}	6095	0.959	.135429	.120465	.166082	.179510
${}^2D_g$	5×10^{-7}	19809	0.955	.157685	.153366	.168271	.183055
${}^2D_g$ SCF orbitals (energy offset $-1639\, E_H$)							
${}^2S_g$	5×10^{-6}	9043	0.954	.211420	.193666	.238712	.255509
${}^2S_g$	5×10^{-7}	27246	0.952	.234233	.229611	.242119	.259790
${}^2D_g$	5×10^{-6}	5075	0.951	.164547	.157880	.175433	.192648
${}^2D_g$	5×10^{-7}	12684	0.950	.174068	.172741	.176211	.193778

[a] The size of a complete SDCI amounts to 317346 CSF's (${}^2S_g$) and 319376 CSF's (${}^2D_g$)

[b] including a multireference analog of the Davidson correction

frozen core effect at the nonrelativistic level. An MCPF treatment based on a constrained SCF for ^2D_g, in which the argon core was frozen to averaged ^2S_g–^2D_g orbitals but the $4s$ and $3d$ orbitals were relaxed, yields only slightly higher energies than the corresponding MCPF using fully optimized ^2D_g SCF orbitals. This implies that relaxation of the valence orbitals is important for the states with d^9 occupation but that this relaxation cannot be achieved by single excitations in the CI step. In the basis of ^2S_g orbitals, at least triple excitations are needed to reorganize the valence orbitals.

On the basis of the experience, that the total CI energies of the d^{10} states are lower if ^2D_g SCF or CAS4 orbitals are employed as compared to ^2S_g SCF orbitals, we have also calculated the ^2S_g state using ^2D_g CAS*mix* orbitals as one-particle set. To this end, the reference set determined from the ^2S_g CAS11 expansion was augmented by single excitations yielding a total of 31 reference configurations in 18 active orbitals. The MRD-CI energy based on ^2D_g CAS*mix* orbitals ($-1639.231747\ E_H$) is considerably higher than the energy obtained for the ^2S_g CAS11 orbitals ($-1639.246601\ E_H$) using the same reference set. We conclude that when using this type of orbitals, in which radial $3d$ correlation is already accounted for in the CAS step, every state should be calculated in its own set of orbitals.

Let us now turn to a comparison of AO bases A and B. Since the basis sets differ in many respects, we will try to analyze the differences step by step. The contraction of the s and p sets has no influence on the correlation energy both in the nonrelativistic as well as in the no-pair calculations. The additional s function (exponent 0.33) and the more compact outermost p functions contained in basis A stabilize preferentially the ^2D_g state. At the nonrelativistic SDCI level, the differential effect on the ^2D_g excitation energy due to these basis functions amounts to -0.14 eV if in basis B only the proper angular momentum components of d and f functions are retained. The gaps in the s and p sets of basis B are filled, however, by the s- and p-type combinations of the cartesian d and f functions. Although this way of compensating basis set deficiencies saves time in the integral evaluation step, it cannot be recommended generally since great care is required to avoid linear dependencies. Apart from a systematic shift of the ^2P_u ($d^{10}p^1$) state, the excitation energies calculated in bases A and B resemble each other very closely. The ^2S_g ($d^{10}s^1$)–^2P_u ($d^{10}p^1$) separation, is rather insensitive to both the addition of polarization functions and the choice of one-particle basis since there is no differential d-intrashell correlation contribution. For a proper description of the $4p$ orbital in this state a diffuse p function is required, however, which is not present in basis A.

3.4. *Relativistic effects*

Another test for the quality of a calculated wavefunction is the evaluation of properties other than the energy. In the spectrum of the copper atom a striking feature is the large spin-orbit splitting of the ^2D_g state which amounts to $-2042.858\ \mathrm{cm}^{-1}$ experimentally [41]. (The negative sign indicates an inverted state with the larger J-value lowest in energy.) Employing ^2D_g CAS(s, p) orbitals, a first-order spin-orbit splitting of $-2006\ \mathrm{cm}^{-1}$ is obtained in the Breit–Pauli approximation in excellent agreement with experiment. Second-order contributions to the ^2D_g splitting are expected to be small since there are no close-lying *gerade* states with angular momentum $J = 2$. In the following, we will only consider symmetry preserving (kinematical) relativistic effects.

Table 6. Summary of no-pair excitation energies obtained at the MRD-CI level. Energies including a multireference analog of the Davidson correction are given in parentheses

		Experiment[a]	One-Particle Basis (AO basis *A*)				One-Particle Basis (AO basis *B*)		
	State		^2S_g SCF	^2D_g SCF	^2D_g CAS(s,p)	aver. SCF	^2S_g SCF	^2D_g SCF	aver. NOs[b]
Cu	^2S_g $(d^{10}s^1)$	0.00	.35006[c] (.37224)[c]	.36211[c] (.37943)[c]	.36138[c] (.37873)[c]	.35439[c] (.37912)[c]	.82686[c] (.84621)[c]	.83638[c] (.85179)[c]	.82712[c] (.84561)[c]
Cu	^2D_g (d^9s^2)	1.49	1.21 (1.44)	1.29 (1.27)	1.15 (1.19)	1.24 (1.45)	1.21 (1.39)	1.17 (1.16)	1.36 (1.39)
Cu	^2P_u $(d^{10}p^1)$	3.81	3.96 (4.02)	4.08 (4.10)	4.15 (4.14)	3.98 (4.08)	3.86 (3.92)	4.07 (3.97)	3.83 (3.86)
Cu	^4P_u $(d^9s^1p^1)$	4.92	5.03 (5.13)	4.77 (4.83)	4.70 (4.74)	4.76 (4.97)	5.05 (5.12)	4.67 (4.77)	4.67 (4.71)
Cu	^4F_u $(d^9s^1p^1)$	5.12	5.14 (5.27)	5.05 (5.16)	4.86 (4.93)	4.87 (5.09)	5.27 (5.34)	4.92 (5.03)	4.97 (5.01)
Cu	^2F_u $(d^9s^1p^1)$	5.50	5.47 (5.59)	5.29 (5.37)	5.24 (5.28)	5.21 (5.39)		5.33 (5.41)	5.14 (5.17)
Cu	^2P_u $(d^9s^1p^1)$	5.68	5.72 (5.85)	5.32 (5.39)	5.36 (5.41)	5.34 (5.52)			
Cu^+	^1S_g $(d^{10}s^0)$	7.72	7.33 (7.48)	7.42 (7.51)	7.41 (7.50)	7.39 (7.53)	7.46 (7.59)	7.42 (7.52)	7.43 (7.52)

[a] Ref. [41]; energies averaged over fine-structure levels

[b] averaged natural orbitals from an MRD-CI treatment of ^2S_g and ^2D_g in the basis of ^2S_g SCF orbitals

[c] total energies; the energy offset is $-1653\ E_H$

The relativistic orbital relaxation has already been discussed in the SCF section. Relativistic effects on the CI excitation energies are found by comparing the results of the nonrelativistic and the no-pair calculations which are given in Tables 4 and 6, respectively. The relativistic correction to the excitation energy of a given state is found to be nearly constant within the no-pair approximation, irrespective of the particular one-particle basis employed. This is especially noteworthy since in a first-order perturbation approach using the MVD operator the argon core, usually frozen in the correlation treatment, makes important contributions to the excitation energies. A detailed analysis of the orbital expectation values of the MVD operator for both ^2S_g and ^2D_g states (Table 7) shows that the 3*s* and 3*p* orbitals contribute 0.22 eV to the MVD correction, about half of the total MVD correction. The differential effect due to the core electrons is lost in this treatment, of course, if the correlation calculation is performed in a common set of orbital basis or if frozen core orbitals are employed. This is demonstrated by an MCPF treatment in the basis of SCF orbitals optimized under the constraint that the argon core was kept frozen to a ^2S_g–^2D_g average. Although the nonrelativistic excitation energy is not altered in these calculations (Table 3), the first-order MVD correction has shrunk to −0.27 eV, compared to −0.46 eV if no constraints are imposed. The corresponding relativistic energy shift in the no-pair calculations amounts to 0.42–0.43 eV.

The relativistic effect on the ^2D_g excitation energy is by far the largest for all states considered. The ^2P_u ($d^{10}p^1$) state is shifted upwards since the relativistic increase in energy is generally smaller in an *np* shell compared to *ns*. The shift amounts to 0.14 eV in AO basis *A* and is slightly larger (0.18 eV) in AO basis *B* which contains an optimized 4*p* gaussian for this stage. The $d^9s^1p^1$ states are consistently stabilized by 0.2–0.3 eV with respect to the ground state possessing also one *s* electron but fewer *p* electrons. Finally, the calculated ionization energy of copper is increased relativistically by 0.2 eV, a value also obtained in first-order MVD calculations [13].

As stated above, the relativistic effect on the excitation energy of a particular state is almost constant for all one-particle bases tested. This is not true, however, for the averaged NOs. While the differential relativistic decrease of the ^2D_g–^2S_g splitting is reproduced well also in the NO basis, the effects on the states

Table 7. Orbital contributions to the MVD correction to the ^2S_g ($d^{10}s^1$)–^2D_g (d^9s^2) energy separation

Orbital	$E_{MVD}(^2S_g)$ [E_H]	$E_{MVD}(^2S_g)$ [E_H]	ΔE [eV]	
1*s*	8.8060	8.8056	+0.01	
2*s*	2.2114	2.2111	+0.01	
2*p*	2.4134	2.4128	+0.02	
3*s*	0.3478	0.3520	−0.11	
3*p*	0.3646	0.3701	−0.15	
Core				−0.22 eV
3*d*	0.0729	0.0721	+0.02	
4*s*	0.0069	0.0167	−0.26	
Valence				−0.24 eV
Sum				−0.46 eV

with occupied $4p$ orbitals are erratic. This stems most probably from the fact that the p NOs are $4s$ correlating orbitals and are not well suited to describe a spectroscopic $4p$ orbital.

4. Conclusions

Summarizing our results, we find that the approximate form of the no-pair operator used in this work and its evaluation via a matrix representation in momentum space leads to an orbital description which agrees satisfactorily with those obtained from spin-averaged Dirac–Fock theory. The nonrelativistically optimized $15s11p6d$ basis set is flexible enough to describe also the orbitals in our relativistic treatment. AO basis set contraction errors in the no-pair calculations are found to be of the same size as those in the nonrelativistic treatment.

At the CI level including Davidson correction, the calculated relativistic excitation energy of the ^2D_g atomic state differs from experiment by as much as 0.48 eV if the ground state is treated in the basis of its SCF orbitals and for ^2D_g only $4s^2 \rightarrow 4p^2$ excitations are accounted for in the CASSCF procedure. Inclusion of $3d$ radial correlation in the orbital optimization step improves the excitation energy substantially, but still the experimental value is underestimated by 0.27 eV. Similar results have been obtained previously also for the d^8s^2–d^9s^1 separation in atomic nickel [44]. The best compromise to describe the ^2S_g $(d^{10}s^1)$, ^2D_g (d^9s^2), ^2P_u $(d^{10}p^1)$, $^{2,4}\{F, P\}_u$ $(d^9s^1p^1)$, and ^1S_g (d^{10}) state of neutral and ionic copper in a common set of one-particle basis is to use d^9 orbitals with near-degeneracy effects accounted for in the orbital optimization step. The ^2S_g–^2D_g separation obtained in this orbital basis (0.30 eV) is only slightly inferior to our best result. The excitation energies of the higher lying $d^9s^1p^1$ states and the first ionization potential agree with experiment to within 0.2 eV. In addition to the $4p$-polarization functions commonly used in studies of copper compounds, the $d^{10}p^1$ state needs at least one diffuse p function.

In the no-pair approximation, differential relativistic effects are found to be nearly independent of the one-particle basis employed. This makes it possible to employ a frozen argon core in the variational calculations in contrast to mass-velocity and Darwin first-order perturbation treatments, for which the $3s$ and $3p$ core electrons contribute considerably to the relativistic change in the excitation energies. The Breit–Pauli form of the spin-orbit operator is still a good approximation for third row elements. The first-order spin-orbit splitting of the ^2D_g state ($-2006\ \mathrm{cm}^{-1}$) is in excellent agreement with the experimental value.

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