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Direct relativistic MP2: properties of ground state CuF, AgF and AuF

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Abstract. A computer program for the calculation of the MP2 energy correction for a Kramers-restricted Dirac-Hartree-Fock four component wave-function is presented. In the spirit of the integral-driven direct SCF scheme the algorithm has been developed as direct MP2, calculating integrals as they are needed and avoiding the integral storage bottle-neck of conventional MP2. Relativistic MP2 is applied to ground state ($^1\Sigma^+$) CuF, AgF and AuF.

Key words: Direct methods – Relativistic effects – MP2 – Ground state properties: CuF, AgF, AuF

1 Introduction

Over the last 10 years there has been a steady development of methods and software for four-component relativistic calculations for molecules. Today there are a number of codes available [1–7] that can perform Dirac-Hartree-Fock (DHF) calculations for general polyatomic molecules using standard quantum chemical approaches based on an analytic expansion of the wavefunction in a finite basis set. These DHF calculations are extremely useful for calibration purposes and also give realistic descriptions of some molecular systems. In general, however, the independent particle approximation inherent in the DHF approach has the same shortcomings as for the non-relativistic (NR) case, and one needs to look beyond this for methods that account for electron correlation.

The first successful approach to a four-component treatment of correlation in polyatomic molecules was implemented in the relativistic CI code in MOLFDIR [8, 9]. However, the spin-orbit coupling in systems containing heavy atoms frequently leads to problems associated with near degeneracies and non-dynamical correlation effects, and thus a multiconfiguration approach along the lines of the non-relativistic MC SCF methods is really required for an adequate treatment of some of these systems. The principles of multiconfiguration DHF (MC DHF) calculations have been discussed in recent work by Jensen et al. [10].

Unfortunately, four-component CI and MC DHF calculations will be very costly even with greatly reduced active spaces, and it is therefore of interest to investigate also other approaches to a relativistic treatment of correlation. For molecules where a single reference DHF wavefunction yields a reasonable description of the ground state, coupled cluster (CC) methods provide an attractive alternative for the treatment of dynamical correlation [11, 12]. Very accurate results are obtained in these CC calculations, but again these are rather expensive and place high demands on computational resources. A cheaper approach at a less accurate level than CC is provided by second-order Møller-Plesset perturbation theory (MP2) [13], which has been applied by Dyall for Kramers-restricted DHF reference wavefunctions (RMP2), both for closed and open shell systems [14].

One advantage of the MP2 approach is that it is possible to implement it in an integral-driven direct version. For non-relativistic quantum chemistry, direct methods with recalculation of two-electron integrals have been used in calculations on large systems where the storage and retrieval of a large number of integrals would constitute a major bottleneck [15–17]. This becomes even more crucial for relativistic calculations where the number of integrals increases as a consequence of the increase in the number of basis functions required to describe both large and small spinor components in a balanced fashion [18, 19]. The advantages of direct algorithms for DHF calculations have been demonstrated in recent applications by Saue and coworkers [7].

In this work we extend the direct approach to RMP2 calculations, and describe the implementation of a Kramers-restricted RMP2 algorithm for general molecular calculations. In the next section we briefly summarize the theoretical foundation of the Kramers-restricted RMP2. On the basis of this we describe an algorithm for such calculations and discuss its implementation

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(Sect. 3). We then present computational results obtained in the application of direct RMP2 in calculations on the ground states ($^1\Sigma^+$) of the coinage metal fluorides – CuF, AgF and AuF.

2 Theory

The second quantized NR Hamiltonian in terms of spin-orbitals and the Dirac-Coulomb (DC) Hamiltonian in terms of molecular spinors have the same form,

$$H = \sum_{pq} \langle p|\, h\, |q\rangle p^\dagger q + \frac{1}{2}\sum_{pqrs} \langle pq|\, g\, |rs\rangle p^\dagger q^\dagger sr. \tag{1}$$

The summation in the DC expression is restricted to electron solutions only. This corresponds to the no-pair approximation, which is an implicit projection of the Hamiltonian onto the positive energy space, so that creation of virtual positron-electron pairs is neglected. In the relativistic expression the operator h is the one-electron Dirac Hamiltonian described in standard textbooks [20, 21]. The Coulomb operator g is the zeroth order approximation (in terms of the fine structure constant) to the fully relativistic frequency dependent electron-electron interaction. Higher-order terms in this expansion arising from the Breit (or Gaunt) interaction are not considered in this work.

Owing to the formal similarity of the Hamiltonians in the non-relativistic and relativistic case, the methods for treating correlation may be transferred directly from the NR case. The MP2 [13] energy expression is

$$E^{(2)} = \frac{1}{4}\sum_{IJAB} \frac{|(IA|JB) - (IB|JA)|^2}{\varepsilon_I + \varepsilon_J - \varepsilon_A - \varepsilon_B} = \frac{1}{4}\sum_{IJAB} \frac{|\langle IJ \| AB\rangle|^2}{\varepsilon_I + \varepsilon_J - \varepsilon_A - \varepsilon_B} \tag{2}$$

both in non-relativistic and relativistic theory. Here we have introduced the anti-symmetrized two-electron integrals, and the integrals $(IA\,|\,JB)$ are given in Mulliken notation. The two-electron integrals, which are expressed in terms of spin-orbitals in NR theory, refer to molecular four-spinors in relativistic theory. Indices I and J refer to occupied spinors and A and B to virtual spinors.

The NR reduction of the MP2 energy in terms of spin-orbitals to a sum over real molecular (space) orbitals may be found in standard textbooks [22]. Owing to spin function orthogonality, the expression in Eq. (2) simplifies to

$$E^{(2)}_{NR} = \sum_{ij}\sum_{ab} \frac{1}{D_{ijab}} \{(ia\,|\,jb)(2(ai\,|\,bj) - (bi\,|\,aj))\}, \tag{3}$$

where we introduce

$$\frac{1}{D_{ijab}} = \frac{1}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} \tag{4}$$

as a convenient notation for the energy denominator. The computational evaluation of this energy expression involves a four-index transformation of two-electron integrals from a basis of real atomic functions (AO-basis) to real molecular orbitals (MO-basis)

$$(ia\,|\,jb) = \sum_{pqrs} C_{pi} C_{qa} C_{rj} C_{sb} (pq\,|\,rs). \tag{5}$$

In relativistic theory the inclusion of time-reversal symmetry introduces Kramers pairs of molecular spinors $(\phi_i, \overline{\phi}_i)$, the relativistic equivalents of molecular spin-orbitals $(\phi_{i\alpha}, \phi_{i\beta})$. However, the convenient spin orthogonality of the NR case is lost, as there is no general orthogonality between opposite members of different Kramers pairs, e.g. ϕ_i and $\overline{\phi}_j$ when $i \neq j$. The four-component molecular spinor ϕ_i is in general complex, but may be expanded in sets of real scalar basis functions $[\chi^L]$ and $[\chi^S]$ for the large and small components respectively, chosen to satisfy the appropriate conditions of kinetic balance [18, 19],

$$\phi_i = \begin{pmatrix} \phi_i^{L\alpha} \\ \phi_i^{L\beta} \\ i\phi_i^{S\alpha} \\ i\phi_i^{S\beta} \end{pmatrix} = \begin{pmatrix} \sum_p \chi_p^L C_{pi}^{L\alpha} \\ \sum_p \chi_p^L C_{pi}^{L\beta} \\ i\sum_q \chi_q^S C_{qi}^{S\alpha} \\ i\sum_q \chi_q^S C_{qi}^{S\beta} \end{pmatrix}. \tag{6}$$

Operation on the spinor with the time reversal operator $\hat{K}$ generates the Kramers partner of ϕ_i,

$$\hat{K}\phi_i = \overline{\phi}_i = \begin{pmatrix} \sum_p \chi_p^L C_{p\bar{i}}^{L\alpha} \\ \sum_p \chi_p^L C_{p\bar{i}}^{L\beta} \\ i\sum_q \chi_q^S C_{q\bar{i}}^{S\alpha} \\ i\sum_q \chi_q^S C_{q\bar{i}}^{S\beta} \end{pmatrix} = \begin{pmatrix} \sum_p \chi_p^L \left(-C_{pi}^{L\beta^*}\right) \\ \sum_p \chi_p^L \left(C_{pi}^{L\alpha^*}\right) \\ i\sum_q \chi_q^S \left(C_{qi}^{S\beta^*}\right) \\ i\sum_q \chi_q^S \left(-C_{qi}^{S\alpha^*}\right) \end{pmatrix}. \tag{7}$$

As pointed out above, unlike the molecular spin-orbitals in NR theory, the barred and unbarred spinors are not in general orthogonal. The reduction of the sum over spinors in Eq. (2) into a sum over Kramers pairs gives the expression

$$\begin{aligned} E_R^{(2)} = \frac{1}{2}\sum_{j\leq i}\sum_{b\leq a} (2-\delta_{ij})(2-\delta_{ab}) \frac{1}{D_{ijab}} (&|\langle ij \,\|\, ab\rangle|^2 \\ &+ |\langle \bar{i}j \,\|\, ab\rangle|^2 + |\langle \bar{i}\bar{j} \,\|\, ab\rangle|^2 + |\langle ij \,\|\, \bar{a}b\rangle|^2 \\ &+ |\langle ij \,\|\, a\bar{b}\rangle|^2 + |\langle \bar{i}\bar{j} \,\|\, a\bar{b}\rangle|^2 + |\langle ij \,\|\, \bar{a}\bar{b}\rangle|^2 \\ &+ |\langle \bar{i}\bar{j} \,\|\, \bar{a}b\rangle|^2), \end{aligned} \tag{8}$$

in terms of anti-symmetrized two-electron integrals. The molecular orbital two-electron electron repulsion integrals (MO ERI) are expanded in real atomic basis functions,

$$\begin{aligned} (ia\,|\,jb) &= \sum_{XY}\sum_{\sigma\gamma}\sum_{pqrs} C_{pi}^{X\sigma^*} C_{qa}^{X\sigma} C_{rj}^{Y\gamma^*} C_{sb}^{Y\gamma} (pq|rs), \\ (\bar{i}a\,|\,jb) &= \sum_{XY}\sum_{\sigma\gamma}\sum_{pqrs} \mathrm{sign}(X,\sigma) C_{pi}^{X\,\mathrm{opp}(\sigma)} C_{qa}^{X\sigma} C_{rj}^{Y\gamma^*} C_{sb}^{Y\gamma} (pq|rs). \end{aligned} \tag{9}$$

Here X,Y denote *Large, Small* and σ, γ denote α, β, and the following conventions are used:

$$\mathrm{sign}(X,\sigma) = \begin{cases} -1 & \text{if (X = L and } \sigma = \alpha\text{) or} \\ & \text{(X = S and } \sigma = \beta\text{)} \\ 1 & \text{else} \end{cases}$$

$$\mathrm{opp}(\sigma) = \begin{cases} \alpha & \text{if } \sigma = \beta \\ \beta & \text{if } \sigma = \alpha \end{cases} .$$

The types of two-electron integrals over scalar basis functions needed in the calculation are $(LL|LL)$, $(LL|SS)$ and $(SS|SS)$ where L and S denote a function from the sets $[\chi^L]$ and $[\chi^S]$ respectively. The other integral types in Eq. (8) give similar expressions to those in Eq. (9) and are easily deduced from the equations above. As described by Dyall [14], several of these integral types give no contribution for certain point group symmetries. In the present work we have not exploited possible computational savings owing to symmetry, and all molecular integrals are calculated.

3 Implementation

The bottleneck in the MP2 calculation is the transformation of scalar two-electron atomic orbital electron repulsion integrals (AO ERI) to MO ERI over molecular orbitals in Eq. (5) or molecular spinors in Eq. (9). In the simplest conventional MP2 scheme, the AO ERI are stored on disk and the transformation performed in four successive 1/4-transformations. The first transformation is the most expensive, and the computational cost is ON^4, where N is the number of basis functions and O the number of electrons in the occupied space.

Compared with the NR calculation the four-index transformation in the RMP2 calculation is more expensive owing to several factors:

1. The algebra involved is complex
2. A total of 8 different types of integrals are needed as seen from Eq. (8).
3. The spinors have four components.
4. For the same type of system, the relativistic calculations employ larger basis sets owing to the need to include the small components and the requirement of kinetic balance. [7, 19, 23].

To avoid the integral storage bottleneck in the conventional MP2 scheme, algorithms for direct and semidirect MP2 have been developed by Head-Gordon et al. [16] and by Sæbø and Almöf [17]. In a slightly modified scheme, the algorithm in [16] may be schematically described as:

```
Loop over batches of MO $I,J$
  Calculate AO ERI
  Transform of 3/4-transformed ERI
  Accumulate in MP2 energy ($E^{(2)}$)
End Loop.
```

The size of the batches of I and J is determined by the available memory. Large calculations may be feasible by splitting up the calculation in several batches with size I, whereas smaller calculations may be performed with a single batch of occupied MO.

The relativistic algorithm used by us in the present work is slightly more complicated as $E^{(2)}$ must be calculated from molecular four-spinor (MS) ERI

(Scheme 1):

```
Loop over types $(LL|LL)$, $(LL|SS)$ and $(SS|SS)$
  Loop over batches of MS $I,J$
    Calculate AO ERI and transform
    Accumulate in MS array
End Loops
Calculate $E^{(2)}$.
```

A detailed description of the Kramers-restricted direct RMP2 algorithm is given in Fig. 1. Instead of adding ERI contributions directly to $E^{(2)}$, the ERI are accumulated in an MS array with size of order O^2V^2(V is the number of virtual positive energy spinors). As in the NR direct MP2 algorithm of Head-Gordon et al. [16], the loop over R,S-shells is not closed until after the 3/4-transformation. This prevents the exploitation of the permutational symmetry $(pq|rs) = (rs|pq)$ of the AO ERI, and the integrals therefore have to be calculated twice for every batch of occupied spinors. This is also the reason why the relativistic scheme stores the MS array in internal memory as it is then simple to exploit the $(SS|LL)/(LL|SS)$ symmetry of the integrals.

Changing the order of the two outer loops (Scheme 2) gives a less memory-demanding scheme at the cost of having to calculate both the $(SS|LL)$- and $(LL|SS)$-integrals, and this is therefore a choice between a memory- and CPU-demanding scheme. An advantage of the direct MP2 scheme of Head-Gordon et al. [16] is that it is fairly easy to parallelize the algorithm efficiently, as shown recently by Nielsen and Seidl [24]. For a relativistic parallel code with limited internal memory on each node, Scheme 2 would possibly be the best choice.

Scheme 1 has a limiting memory requirement of $I^2V^2 + I^2VN$, where $I = O$ if sufficient memory is available to perform the calculation with only one $I,J-$batch. After the array of MS ERI has been completed, the contribution to the MP2-energy from this batch of molecular spinors is easily calculated, a step that is fast and very cheap compared to the four-index transformation.

As long as one is not doing extremely accurate correlated calculations of chemical properties, only the valence and sub-valence electrons need be considered. In relativistic calculations one is frequently interested in systems containing heavy elements, and for such systems the core electrons often constitute the larger part of the total number of electrons in the system. The elimination of these core electrons from the active space in correlated calculations significantly reduces the size of the calculation.

The algorithm described in Fig. 1 has been implemented in a computer program, and the program has been tested by comparing calculations on small molecules such as CH_4 and HF in the NR limit with corresponding calculations carried out using the NR program GAMESS-UK [25]. Results in the NR limit have been

```
                                                                                              Memory          Flops for
Loop over X,Y (XY = LL, LS and SS)                                                                            batch
    Loop over index for batches I,J of occ. Kramers pairs i, $j \leq$ i (all for LS)                          of I,J
        Loop over R,S shells (Shell size M)
            Loop over p, q (All) and r, s ($\in$ R,S)
                Calculate $(\kappa_p^X \kappa_q^X \mid \kappa_r^Y \kappa_s^Y)$, p$\geq$q, r$\geq$s           $N^2M^2$        $TN^4$
            End Loop
            Loop over p, q, r $\in$ R, s $\in$ S, (p$\geq$q, r$\geq$s)
                Loop over i $\in$ I, $\sigma$ (Spin)
                    $(i^{X\sigma}\kappa_q^X \mid \kappa_r^Y \kappa_s^Y) = (i^{X\sigma}\kappa_q^X \mid \kappa_r^Y \kappa_s^Y) + C_{pi}^{X\sigma^*}(\kappa_p^X \kappa_q^X \mid \kappa_r^Y \kappa_s^Y)$
                    $(i^{X\sigma}\kappa_p^X \mid \kappa_r^Y \kappa_s^Y) = (i^{X\sigma}\kappa_p^X \mid \kappa_r^Y \kappa_s^Y) + C_{qi}^{X\sigma^*}(\kappa_p^X \kappa_q^X \mid \kappa_r^Y \kappa_s^Y)$
                    Do also $(\bar{i}^{X\sigma}\kappa_q^X \mid \kappa_r^Y \kappa_s^Y)$                       $INM^2$         $IN^4$
                End Loop
            End Loop
            Loop over $\sigma$ (Spin), r $\in$ R, s $\in$ S, (r$\geq$s)
                Loop over all a, q, i $\in$ I
                    $(i^X a^X \mid \kappa_r^Y \kappa_s^Y) = (i^X a^X \mid \kappa_r^Y \kappa_s^Y) + C_{qa}^{X\sigma}(i^{X\sigma}\kappa_q^X \mid \kappa_r^Y \kappa_s^Y)$
                    Do also $(\bar{i}^X a^X \mid \kappa_r^Y \kappa_s^Y)$ , $(i^X \bar{a}^X \mid \kappa_r^Y \kappa_s^Y)$                       $IVN^3$
                End Loop
                Loop over $\gamma$, a, i $\in$ I, j $\in$ J
                    $(i^X a^X \mid j^{Y\gamma}\kappa_s^Y) = (i^X a^X \mid j^{Y\gamma}\kappa_s^Y) + C_{rj}^{Y\gamma^*}(i^X a^X \mid \kappa_r^Y \kappa_s^Y)$
                    $(i^X a^X \mid j^{Y\gamma}\kappa_r^Y) = (i^X a^X \mid j^{Y\gamma}\kappa_r^Y) + C_{sj}^{Y\gamma^*}(i^X a^X \mid \kappa_r^Y \kappa_s^Y)$
                    Do also $(\bar{i}^X a^X \mid j^{Y\gamma}\kappa_s^Y)$ , $(i^X \bar{a}^X \mid j^{Y\gamma}\kappa_s^Y)$
                    $(i^X a^X \mid \bar{j}^{Y\gamma}\kappa_s^Y)$ , $(i^X \bar{a}^X \mid \bar{j}^{Y\gamma}\kappa_s^Y)$               $I^2VN$         $I^2VN^2$
                End Loop
            End Loop
        End Loop over R,S
        Loop over $\gamma$, i $\in$ I, j $\in$ J, a, b, s
            $(ia \mid jb) = (ia \mid jb) + C_{sb}^{Y\gamma}(i^X a^X \mid j^{Y\gamma}\kappa_s^Y)$
            Accumulate also $(\bar{i}a \mid jb), (i\bar{a} \mid jb), (ia \mid \bar{j}b), (ia \mid j\bar{b})$,
                $(i\bar{a} \mid \bar{j}b), (ia \mid \bar{j}\bar{b}), (i\bar{a} \mid j\bar{b})$                       $I^2V^2$        $I^2V^2N$
        End Loop
    End Loop over I,J
End Loop over X,Y
Calculate $E^{(2)}$
```

n_i : Number of batches of I
Total execution time is of the order n_i^2
TN^4: Flops for integral evaluation
N : Total number of basis functions (L or S)
I : Size of largest I batch = Size of largest J batch
V : Size of virtual space

Fig. 1. Algorithm (scheme 1) for direct relativistic MP2 (RMP2) with order of magnitude estimates of memory requirements and floating point operations in each step

obtained from the relativistic program by setting a large value (10^4 in atomic units) for the speed of light. As in DIRAC [7], the integrals are calculated with the HERMIT program [26]. The direct RMP2 program is now running on IBM RS6000 workstations, and all the calculations have been performed on IBM RS6000 590 and 990 workstations.

With the present implementation of the RMP2 the total time needed for the RMP2 calculation is of about the same as for the total DHF calculation. Work is now in progress to upgrade the program to take advantage of the point group symmetry of the molecules. It is expected that this will speed up the calculations significantly, and the RMP2 calculation should eventually require only a small fraction of the CPU time for the full direct DHF calculation.

4 Calculations

Pyykkö and Desclaux [27] have pointed out that for a given row of the periodic system, relativistic effects on bond lengths and vibrational frequencies appear to be largest for the coinage metals (the 'gold maximum'). The usual explanation is the important 6*s* contribution to the bonding of Au and the contraction of the *s*-spinors owing to relativity and inefficient screening by the 5*d*-electrons. The contraction of the *s*-spinors is greater than the contraction of spinors belonging to other symmetries. This would appear to make the coinage metal halides an interesting testing ground for relativistic MP2 calculations. In this work we have studied the fluorides CuF, AgF, and AuF. The properties of the ground state hydrides have already been investigated with similar methods by Collins et al. [28].

Coinage metal fluorides have been studied previously by a number of investigators using various theoretical models. Thus CuF has been the subject of CISD and Møller-Plesset perturbation calculations to fourth order (MP4) with near-Hartree-Fock limit basis sets by Schwerdtfeger et al. [29] and MRCI calculations by Ramírez-Solís and Daudey [30]. Ramírez-Solís and Schamps [31] have studied AgF using the pseudopotential method with a high quality valence basis set and an MRCI-MP2 treatment of correlation. For AuF pseudopotential calculations have been performed by Schwerdtfeger et al. [32–34]. These calculations use high-quality valence basis set and also include correlation by many-body perturbation theory (MP2, MP3 and MP4) and single reference CCSD and CCSD(T). Correlation effects have thus already been studied at a high level of theory for these compounds, but the relativistic effects have only been accounted for through relativistic pseudopotentials [30–34] or a first-order perturbation estimate of the mass-velocity and Darwin terms (MVD-approximation) [29]. In this study we present calculations for the ground state ($^1\Sigma^+$) of CuF, AgF and AuF using moderately sized basis sets in fully relativistic DHF calculations, and with correlation treated at the MP2-level.

4.1 Computational details

Basis sets of dual family type were optimized for the coinage metal atoms using the non-relativistic program TANGO [35]. One (Cu, Ag) or two (Au) high-exponent *p*-functions were added to give a better description of the $2p_{\frac{1}{2}}$ spinor. These additional exponents were optimized using a simple stepwise search and the program GRASP [36] modified for basis set calculations [3] for the atomic configuration $(n-1)d^{10}ns^1$ of the atoms. The basis sets were supplemented with 2 (Cu, Ag) or 3 (Au) diffuse *p*-functions, 1 *d*-function and 3 (Cu), 4 (Ag) or 2 (Au) *f*-functions. With these basis sets the deviation of the energy from the relativistic Hartree-Fock limit was $15.6 \cdot 10^{-3}$ a.u., $16.0 \cdot 10^{-3}$ a.u. and $125.8 \cdot 10^{-3}$ a.u. for Cu, Ag, and Au respectively.

The bond in the coinage metal fluorides in strongly polar owing to the large electronegativity of fluorine. To obtain a basis set that could describe the strong polarization in the molecule, a fluorine 9*s*6*p* basis set was optimized using TANGO [35] for the negative ion F^- and augmented with 2*d*-functions. Test MP2 calculations on LiF showed this to be a balanced basis set and that more *d*-functions gave no significant improvement in the energy.

The Cartesian Gaussian basis sets have been used uncontracted and have final sizes for the large component basis of 16*s*14*p*9*d*3*f* (Cu), 20*s*17*p*12*d*4*f* (Ag), 22*s*20*p*14*d*10*f* (Au), and 9*s*6*p*2*d* (F) (Tables 1–4). The basis sets for the small (S) components have been generated from the large component sets (L) using the unrestricted kinetic balance condition [7, 23]. The total number of basis functions is 557, 676 and 896 for CuF, AgF and AuF respectively.

For the non-relativistic SCF and MP2 calculations GAUSSIAN 92 [37] was used for CuF and AgF. The NR properties of AuF were calculated with Noga and Klopper's DIRCCR12-95 code [38]. In the relativistic calculations the Kramers-restricted, Dirac-Hartree-Fock closed-shell wavefunctions were generated in the DIRAC [7] program with a direct DHF algorithm. Finite-size Gaussian nuclei were used (Tables 1–4). The exponents for the Gaussian nuclei have been generated as described by Dyall et al. [3].

In the MP2 calculations the active virtual space for correlation was restricted to Kramers pairs with energy less than 100 atomic units (a.u.), giving an active virtual space of 113, 126, 139 Kramers pairs for the 3 systems in the RMP2 calculations. The active occupied space included the 18 valence electrons. Calculations where the subvalence $ns(n-1)p$ spinors were included for a total of 26 electrons in the active space were also performed.

Table 1. Dual family basis set and Gaussian nucleus exponent for Cu. The exponents for *d*- and *f*-functions are marked in the *s*- and *p*-exponent set

Cu, *s* and *p* exponents:	
773890.981	41300.00000
115957.966	6294.85104
26389.7471	1491.72487
7471.91123	483.50607
2434.76613	183.652452
875.567861	76.9761603
337.463142	34.2443702
136.031615 (*d*)	15.8260699
54.9799838 (*d*)	7.38254008 (*f*)
23.0394386 (*d*)	3.31453805 (*f*)
98.847061 (*d*)	1.41929959 (*f*)
4.18791620 (*d*)	0.558513822
1.68470868 (*d*)	0.170000000
0.624808942 (*d*)	0.049000000
0.202890599 (*d*)	
0.052726332 (*d*)	

Gaussian nucleus exponent: $2.76836 \cdot 10^8$

Table 2. Dual family basis set and Gaussian nucleus exponent for Ag. The exponents for *d*- and *f*-functions are marked in the *s*- and *p*-exponent set

Ag, *s* and *p* exponents:	
10170633.2	205000.000
1523109.59	30568.0033
346619.456	7239.55182
98170.8513	2350.55536
32015.7325	897.944491
11539.4904	380.120972
4473.0654	172.659937
1822.98695	82.2017109
768.19299 (*d*)	40.3707460
333.034012 (*d*)	19.7645648
147.079718 (*d*)	9.76105823
64.1605984 (*d*)	4.87962949 (*f*)
29.5320182 (*d*)	2.22809405 (*f*)
13.7938975 (*d*)	0.995074617 (*f*)
6.48144012 (*d*)	0.403846107 (*f*)
2.93475388 (*d*)	0.162000000
1.27714335 (*d*)	0.065000000
0.507816839 (*d*)	
0.178191524 (*d*)	
0.0464943888 (*d*)	

Gaussian nucleus exponent: $2.03996 \cdot 10^8$

Geometry optimization was carried out through stepwise variation of the metal fluorine bond distance. The energy was calculated at several bond lengths around the equilibrium (r_e), and force constants were calculated by a quadratic fit to 3 points at $r = r_e$ and $r = r_e \pm 0.01$ Å . For relativistic AuF with 26 electrons correlated the energy was calculated at r_e and at 3 points with a spacing of 0.02 Å around r_e. The force constant was then calculated from a cubic fit. The

Table 3. Dual family basis set and Gaussian nucleus exponent for Au. The exponents for *d*- and *f*-functions are marked in the *s*- and *p*-exponent set

Au, s and p exponents:			
40388037.5		2250000.00	
6047994.46		320000.000	
1376359.95		60387.3360	
389821.512		14304.8139	
127125.247		4640.21919	
45806.4475		1767.01464	
17736.1093		742.207018	
7209.37728		331.722681	(*f*)
3026.14748	(*d*)	154.856063	(*f*)
1308.48872	(*d*)	74.2153330	(*f*)
582.871920	(*d*)	35.8536792	(*f*)
259.343171	(*d*)	17.3725114	(*f*)
122.675842	(*d*)	8.31276028	(*f*)
59.6823221	(*d*)	3.89830437	(*f*)
29.6374681	(*d*)	1.61232151	(*f*)
14.5077421	(*d*)	0.685303118	(*f*)
6.98044078	(*d*)	0.268436640	(*f*)
3.29945865	(*d*)	0.107370000	
1.40559251	(*d*)	0.042950000	
0.554811826	(*d*)	0.017180000	
0.191053592	(*d*)		
0.047778987	(*d*)		

Gaussian nucleus exponent: $1.422456 \cdot 10^8$

Table 4. Fluorine basis set and Gaussian nucleus exponent. The 9*s*6*p* set is optimized for the ion F$^-$ and the 9*s*6p2*d* set is suitable for calculations in molecules with ionic character

F$^-$, s, p and d exponents:		
13874.6194	63.0771751	2.000
2081.83460	14.4880120	0.8000
474.024179	4.38060140	
134.275393	1.45214460	
43.7173394	0.461546462	
15.7374155	0.126211456	
6.04514678		
1.24305124		
0.339833174		

Gaussian nucleus exponent: $5.35493 \cdot 10^8$

vibrational frequencies were calculated from the force constants and the reduced masses listed by Huber and Herzberg [39].

4.2 *Results and discussion*

The calculated DHF and RMP2 bond lengths (r_e) and vibrational frequencies (ω_e) are presented in Table 5. For comparison we also list results from non-relativistic calculations and experimental results for CuF and AgF. AuF has only very recently been detected [40], and no experimental bond lengths or vibrational frequencies are known to the authors.

Owing to the many low-lying configurations in transition metal atoms, multireference calculations are often required to account for the non-dynamical correlation in transition metal compounds. MRCI calculations by Ramírez-Solís and Daudey [30] and Ramírez-Solís and Schamps [31] have shown that the model $\mathrm{Me}^+((n-1)d^{10})\mathrm{F}^-(2p^6)$ (Me = Cu, Ag) provides a good description of the $X^1\Sigma^+$ ground state of MeF. The CI-coefficient for this configuration was found to be 0.97 (CuF) [30] and 0.98 (AgF) [31], and one should not expect any dramatic changes in the correlation contributions for AuF. Non-dynamical correlation should therefore be of minor importance for these systems, and we expect the single reference MP2 method to account for the bulk of the correlation energy in the active space. This is supported by comparison with the AuF pseudopotential calculations by Schwerdtfeger et al. [34] where MP2 results are compared with high-quality treatment of correlation at the CCSD(T)-level.

The DHF calculations were always performed with all ERI included. Neglecting the $(SS|SS)$ ERI in RMP2 calculations on AuF and AgF with 16 valence electrons in the active space gave a vertical shift in the calculated potential energy curve of $0.56 \cdot 10^{-6}$ a.u. for AuF and $0.39 \cdot 10^{-6}$ a.u. for AgF, but had no effect on the shape of the curve. This demonstrates that leaving out the $(SS|SS)$ integrals in RMP2 calculations has a negligible effect on the calculated bond lengths and vibrational frequencies. The remaining RMP2 calculations were therefore performed without the $(SS|SS)$ ERI.

Our results are not corrected for basis set superposition errors (BSSE). A counterpoise correction calculation [41] requires open shell facilities that at present are

Table 5. Calculated bond lengths (r_e) and vibrational frequencies (ω_e) for the ground state ($X^1\Sigma^+$) of CuF, AgF and AuF. The experimental results are from Huber and Herzberg [39]. The vibrational frequencies are calculated from the theoretical force constants and the reduced masses from [39]. Experimental values for AuF are not known to the authors

	Number of electrons correlated	r_e (Å)	ω_e (cm^{-1})
CuF			
NR SCF		1.823	563
NR MP2	18	1.754	606
NR MP2	26	1.751	612
R DHF		1.805	572
R MP2	18	1.728	627
R MP2	26	1.725	633
Exp. [39]		1.745	623
AgF			
NR SCF		2.069	472
NR MP2	18	2.033	491
NR MP2	26	2.026	496
R DHF		2.029	491
R MP2	18	1.987	515
R MP2	26	1.977	521
Exp. [39]		1.983	513
AuF			
NR SCF		2.146	443
NR MP2	18	2.113	458
NR MP2	26	2.103	463
R DHF		1.968	528
R MP2	18	1.916	571
R MP2	26	1.899	590

not implemented in our program. Collins et al. [28] have investigated the effect of BSSE in calculations on the hydrides of the coinage metals. Using the counterpoise method they found that the BSSE is negligible at the SCF level, but gives bond lengths that are 0.01–0.02 Å too short and vibrational frequencies that are up to 1.5% too high for the MP2 calculations. The basis sets used in this work are comparable to theirs in size and quality, but were used uncontracted. We expect the BSSE to be of similar magnitude in our calculations because the greater flexibility in our uncontracted basis sets is mainly in the core. For MP2 a basis set with more valence region flexibility would be required to reduce BSSE, unfortunately the experimentation with larger sets is beyond our present computational resources.

We performed MP2 calculations with 18 (valence) as well as 26 (valence + subvalence) electrons in the active occupied space. In the large occupied space the 8 $(n-1)s^2(n-1)p^6$ subvalence electrons were added to the 18 valence electrons. In relativistic AuF the 14 $4f$-electrons have a higher energy than the $5s$ electrons, but these were not included in the active space. As can be seen from Table 5 the extension of the active space to include the 8 subvalence electrons gave a significant change in the calculated properties, especially for relativistic AuF.

The differential relativistic effects as manifested in these molecules are presented in Table 6. These effects are defined through the formula $\Delta_R P = P^R - P^{NR}$ for the property P, and we expect them to be quite insensitive to BSSE. Collins et al. [28] used basis sets of the same quality as ours and found BSSE for the coinage metal hydrides to be less than 0.005 Å for $\Delta_R r_e$ and 1% for $\Delta_R \omega_e$. The calculated relativistic bond contractions in Table 6 are slightly larger for the MP2 than for the SCF calculations, and this is an example of the well-known non-additivity of relativistic and correlation effects (See e.g. [28]). Using pseudopotential methods for AuF, Schwerdtfeger et al. [34] have calculated the relativistic effects on the bond length to 0.163 Å at the SCF level and to 0.184 Å at the MP2 level. For the force constants their $\Delta_R k_e$ is 0.76 mdyn /Å and 0.92 mdyn/Å. These results may be compared with our fully relativistic calculations which give the relativistic effect as 0.178 Å and 0.204 Å for the bond length and 0.84 mdyn/Å (85 cm^{-1}) and 1.36 mdyn/Å (127 cm^{-1}) for the force constants. The fully relativistic calculation gives slightly larger $\Delta_R P$ for both properties, but the calculations are not directly comparable owing to the difference in the description of the wavefunctions.

Table 6. Relativistic effects for ground state ($X^1\Sigma^+$) CuF, AgF and AuF at SCF and MP2 level (core or core and subvalence frozen). Bond length contraction $\Delta_R r_e$ in Å. Change in vibrational frequencies $\Delta_R \omega_e$ in cm^{-1} and % of relativistic value

	SCF		MP2 18 electr. active		MP2 26 electr. active	
	$\Delta_R r_e$	$\Delta_R \omega_e$	$\Delta_R r_e$	$\Delta_R \omega_e$	$\Delta_R r_e$	$\Delta_R \omega_e$
CuF	−0.018	9 (2%)	−0.026	21 (3%)	−0.026	21 (3%)
AgF	−0.040	19 (4%)	−0.046	24 (5%)	−0.049	25 (5%)
AuF	−0.178	85 (16%)	−0.197	113 (20%)	−0.204	127 (22%)

It is also interesting to compare our results with the very similar calculations by Collins et al. [28] on the coinage metal hydrides. For AuH there is a relativistic contraction of the bond length of 0.261 Å at the DHF level, which is reduced to 0.214 Å for the MP2 result. For AuF we have the opposite effect of correlation since the contraction is increased from 0.178 Å (DHF) to 0.204 Å (MP2). Schwerdfeger et al. have analyzed the relativistic contraction of the bondlength in 14 different diatomic gold compounds at the SCF level and found an almost linear relationship between the relativistic contraction and the Pauling electronegativity of the ligand [32]. The opposite effects of correlation for AuF and AuH results in a much smaller difference in $\Delta_R r_e$ for the two diatomics at the MP2 level than for the uncorrelated calculation. The mechanisms behind this are not immediately clear. We note that at the non-relativistic level MP2 reduces the bond distance by 0.12 Å for AuH but only by 0.04 Å for AuF, while at the relativistic level, the effect of MP2 correlation is a bond contraction of 0.07 Å for both molecules. One interpretation is that with the strong relativistic contraction of the Au electron distribution the correlation of the Au electrons becomes dominant, irrespective of ligand, and that this is reflected in the similar MP2 contractions of the bond length. However, the similarity might also be coincidental, and owing to completely different correlation mechanisms, e.g. charge transfer excitations onto Au, which would be of greater importance for AuF than for AuH. With our present versions of the computer programs, we have no possibility of carrying out a closer investigation of this at the relativistic level, and we feel that no conclusions should be drawn about this from a comparison at the non-relativistic level. A program version presently under development and scheduled for production in late 1997 will have more advanced facilities for wavefunction analysis. It would certainly be interesting to investigate the effect of correlation on relativistic bond lengths for other gold compounds; unfortunately, this falls outside the scope of the present work.

5 Conclusion

We have presented an algorithm for the calculation of the energy correction from second-order perturbation theory for a Kramers-restricted Dirac-Hartree-Fock four-component wavefunction. The algorithm has been developed in the spirit of the integral-driven direct SCF scheme, where electron repulsion integrals are calculated and used as they are needed, and not stored. This eliminates the integral storage bottleneck encountered in conventional MP2. As in NR calculations, the integral-direct procedures may be successfully applied to calculations that would otherwise be impossible because of limited storage capacity. This is especially true for calculations where flexibility of the basis set is important, and the calculations should be carried out without contraction, for example calculations of NMR parameters and electric field gradients at the nuclei.

A number of high-quality four-component relativistic calculations on molecules have been reported during the last 10 years, but most studies of trends in relativistic effects have been at the SCF level. We have performed calculations for the ground state ($^1\Sigma^+$) of CuF, AgF and AuF, and the comparison of our relativistic bond contraction for AuF at the SCF and MP2 level with earlier calculations on AuH suggests that conclusions drawn at the SCF level may need to be revised if one goes beyond the independent particle model and includes correlation. For the bond lengths and vibrational frequencies of the coinage metal fluorides, there is non-additivity of relativistic and correlation effects. There is also a significant effect of leaving out the subvalence electrons in the correlated space.

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References

1. McLean, AD, Lee YS (1982) In: Carbó R (ed) Current aspects of quantum chemistry 1981 Elsevier, Amsterdam p. 219
2. Visscher L, Visser O, Aerts PJC, Merenga H, Niewpoort W (1994) Comput Phys Commun 81:120
3. Dyall KG, Taylor PR, Faegri K Jr., Partridge H (1991) J Chem Phys 95:2583
4. Mohanty A, Clementi E (1991) Int J Quantum Chem 39:487
5. Matsuoka O (1992) J Chem Phys 97:2271
6. Pisani L, Clementi E (1994) J Comput Chem 15:466
7. Saue T (1996) Ph.D. thesis, University of Oslo
8. Visscher L (1993) Ph.D. thesis, University of Groningen
9. Visscher L, Saue T, Nieuwpoort WC, Faegri K Jr, Gropen O (1993) J Chem Phys 99:6704
10. Jensen HJ Aa, Dyall KG, Faegri K Jr., Saue T (1996) J Chem Phys 104:4083
11. Visscher L, Dyall KG, Lee TJ (1995) Int J Quantum Chem Symp 29:411
12. Eliav E, Kaldor U (1996) Chem Phys Lett 248:405
13. Møller C, Plesset MS (1934) Phys Rev 46:618
14. Dyall KG (1994) Chem Phys Lett 224:189
15. Almlöf JE, Faegri K Jr., Korsell K (1982) J Comput Chem 3:385
16. Head-Gordon M, Pople JA, Frisch MJ (1988) Chem Phys Lett 153:503
17. Sæbø S, Almlöf JE (1989) Chem Phys Lett 154:83
18. Stanton RE, Havriliak S (1984) J Chem Phys 81:1910
19. Grant IP, Quiney HM (1988) Adv At Phys 23:37
20. Rose ME (1961) Relativistic electron theory. Wiley, New York
21. Moss RE (1973) Advanced molecular quantum mechanics. Chapman and Hall, London
22. Szabo AS, Ostlund NS (1989) Modern quantum chemistry. McGrawHill, New York
23. Dyall KG, Faegri K Jr., (1990) Chem Phys Lett 174:25
24. Nielsen IMB, Siedel ET (1996) J Comput Chem 16:1301
25. Guest MF, Kendrick J (1986) *GAMESS* Users Manual, SERC Daresbury Laboratory, CCP1/86/1; Dupuis M, Spangler D, Wendoloski J (1980) NRCC Software Catalog, vol. 1, Program No. G01 (GAMESS); Guest MF, Harrison RJ, van Lenthe JH, van Corler LCH van (1987) Theor Chim Acta 71:117
26. Helgaker T, Taylor PR, Ruud K, Vahtras O, Koch H (1995) HERMIT, a Molecular Integral Program
27. Pyykkö P, Desclaux J (1979) Acc Chem Res 12:276
28. Collins CL, Dyall KG, Schaefer HF III (1995) J Chem Phys 102:2024
29. Schwerdtfeger P, Boyd PDW, Bowmaker GA, Aldridge LP (1990) Struct Chem 17:405
30. Ramírez-Solís A, Daudey JP (1989) Chem Phys 134:111
31. Ramírez-Solís A, Schamps J (1995) J Chem Phys 102:4482
32. Schwerdtfeger P, Dolg M, Schwarz WHE, Bowmaker GA, Boyd PDW (1989) J Chem Phys 91:1762
33. Schwerdtfeger P, McFeaters JS, Stephens RL, Liddell MJ, Dolg M, Hess BA (1994) Chem Phys Lett 218:362
34. Schwerdtfeger P, McFeaters JS, Liddell MJ, Hrûsák J, Schwarz H (1995) J Chem Phys 103:245
35. Faegri K Jr., Almlöf JE (1986) J Comput Chem 7:396
36. Dyall KG, Grant IP, Johnson CT, Parpia FA, Plummer EP (1989) Comput Phys Commun 55:425
37. Frisch MJ, Trucks GW, Head-Gordon M, Gill PMW, Wong MW, Foresman JB, Johnson BG, Schlegel HB, Robb MA, Replogle ES, Gomperts R, Andres JL, Raghavachari K, Binkley JS, Gonzalez C, Martin RL, Fox DJ, Defrees DJ, Baker J, Stewart JJP, Pople JA 1992, Gaussian 92, Revision G.2 Gaussian, Pittsburgh Pa.
38. Noga J, Klopper W (1995) DIRCCR12-95 program; Klopper W, Noga J (1995) J Chem Phys 103:6127
39. Huber KP, Herzberg G (1979) Molecular spectra and molecular structure, IV. Constants of diatomic molecules. Litton, New York
40. Schröder D, Hrûsák J, Tornieporth-Oetting IC, Klapötke TM, Schwarz H (1994) Angew Chem Int Ed Engl. 33:212
41. Boys SF, Bernardi F (1970) Mol Phys 19:553