Theor Chim Acta (1988) 74: 479-491

Theoretica
Chimica Acta

The atomic states of nickel

Charles W. Bauschlicher, Jr[1], Per Siegbahn[2] and Lars G. M. Pettersson[2]

[1] NASA Ames Research Center, Moffett Field, CA 94035, USA
[2] Institute of Theoretical Physics, University of Stockholm, S-113 46 Stockholm, Sweden

(Received December 28, 1987; revised and accepted February 22, 1988

The Ni $3d^94s^1(^3D)$-$3d^{10}(^1S)$ and $3d^94s^1(^3D)$-$3d^84s^2(^3F)$ atomic excitation energies have been computed using large multireference CI wave functions in conjunction with a large ANO basis set. Radial correlation effects in the $3d$ shell are found to be very important and are included using CASSCF wave functions having the $3d$ and correlating $3d'$ orbitals in the active space. The previous discrepancy (0.5 eV) with experiment for the ^3D-^1S excitation is reduced to 0.1 eV when the $3d \rightarrow 3d'$ references are included in the CI. For the ^3F state, the $4s$-$4p$ near degeneracy gives rise to important $4s^2 \rightarrow 4p^2$ excitations in addition to the $3d \rightarrow 3d'$ excitations which are important for the ^3D and ^1S states. Inclusion of only $3d$-$3d'$ correlation in the ^3F and ^3D CI reference spaces yields a ^3F-^3D separation which is in error by 0.12 eV. Addition of the $4s^2 \rightarrow 4p^2$ excitations to the ^3F reference space is estimated to increase the discrepancy with experiment by an additional 0.1 eV.

Key words: Ni atom — Correlation energy — Atomic separations

1. Introduction

The theoretical calculation of the splitting between the $3d^n4s^2$, $3d^{n+1}4s^1$ and $3d^{n+2}$ states of the first-row transition metal atoms has been recognized as a long standing problem of considerable difficulty due to the large correlation energy associated with the $3d$ electrons. In particular, Ni atom has attracted much attention [1-8] due to the near-degeneracy between the $3d^94s^1(^3D)$ and the $3d^84s^2(^3F)$ states for which the lowest J-components are separated by only 0.025 eV [9] with the $^3F\ J=4$ component lower in energy. The splitting computed at the numerical Hartree-Fock (NHF) level, however, is 1.63 eV [10] when relativistic effects are included. The error in the ^3F–$^1S(3d^{10})$ separation is even larger (4.33 eV) at the NHF level (including relativistic effects) [10].

In many applications an accurate relative positioning of the different atomic states is an absolute necessity. A particularly striking example is provided by the dipole moment of NiH $X^2\Delta$, which is extremely sensitive to the correct mixing between Ni $3d^84s^2$ and $3d^94s^1$ in the wave function [11]. A CI wave function [11] biased toward the $3d^94s^1$ state yields a large dipole moment, while one biased toward the Ni $3d^84s^2$ occupation yields a dipole moment more than 2D smaller, with the experimental value [12] being intermediate between these two. A treatment which describes both Ni atom states equally, reproduces the experimental dipole moment and the wave function shows considerable mixing of $3d^84s^2$ and $3d^94s^1$, underlining the importance of an accurate description of the atomic separations to obtain a reliable description of molecular systems. In addition, in Ni^0 complexes (usually referred to as $3d^{10}$), such as $\mathrm{Ni(CO)}_n$, the participation of the Ni $3d^{10}(^1S)$ state has been emphasized. To delineate conclusively the importance of $3d^{10}$ participation, an accurate description of this atomic state becomes necessary.

There has been a great deal of work on the atomic separation in nickel and we review some of the important earlier results. As all the wave functions discussed use L–S coupling, we average the experimental results over J-components. This yields a ^3D ground state, with the ^3F and ^1S states 0.03 and 1.74 eV higher in energy. However, relativistic effects have been shown to have a large differential effect on these states [10]. Thus to compare the theoretical results with experiment, we must include an estimate of these effects. As we show below the differential relativistic effect is almost independent of the level of theory used. Therefore, we have corrected our results and previous results using the relativistic corrections deduced by Martin and Hay [10] based on numerical Hartree–Fock calculations with and without the Darwin and mass-velocity terms included. The corrections are −0.36 for ^3D–^3F and 0.21 eV for ^3D–^1S. The negative sign indicates that the excited ^3F state is lowered relative to the ^3D ground state.

Much of the error at the SCF level disappears in a single-reference singles and doubles excitation CI (SDCI) treatment. Using a large STO basis set and correlating 10 electrons, Bauschlicher et al. [4] found that the error in the ^3D–^3F separation was reduced from 1.66 eV at the SCF level to 0.38 eV at the SDCI level. The ^3D–^1S separation was affected in an equally dramatic way, the SCF error of 2.67 being reduced to 0.78 eV. While the SDCI treatment dramatically reduces the error, the discrepancy with experiment is still very large. If the Davidson correction [13] ($+Q$) is used to estimate the importance of higher excitations, the ^3D–^3F separation is hardly affected (0.01 eV reduction of the error), and while the ^3D–^1S separation is improved by 0.22 eV, the remaining error of 0.56 eV is still quite large. The inclusion of $3s$ and $3p$ correlation effects was found to give a small (0.08 eV) effect at the SDCI + Q level. Using the CEPA-1 approach and a basis which included a $[4f\,3g\,1h]$ polarization set, Werner [5] showed that the computed errors in the ^3F–^1S separation (and presumably the ^3D–^1S separation as well) was not due to basis set limitations. Based upon these two studies [4, 5] it appears that the remaining error is due to deficiencies in the treatment of correlation, such as the underestimation of the higher excitations by the Davidson or CEPA-1 corrections.

In order to avoid some of the limitations of the SDCI approaches, perturbation theory and coupled cluster methods have been applied [6, 7] to the Ni atom separations. Rohlfing and Martin (RM) [6] demonstrated a very erratic convergence in the Møller–Plesset (MP) perturbation series. At the coupled-cluster doubles, CCD, level they obtained excitation energies which are in error by slightly more than those at the SDCI level. Estimating the total singles and triples contribution, however, they find a very large effect (0.46 eV) on the ^3D-^3F separation reducing the error to 0.22 eV. Unfortunately, it is not possible to make the same estimate for the ^1S state. Unlike the SDCI approach, inclusion of the $3s3p$ electrons in the CCD correlation treatment had a sizeable effect: 0.13 eV on the ^3D-^3F separation and 0.22 eV on the ^3D-^1S separation. In addition, including the $3s3p$ correlation increases the differential effect of singles and triples. Thus the treatment used by RM correlating 18 electrons and including an estimate of the singles and triples is in error by only 0.07 eV, with the ^3D state too low in energy. The calculation of the singles and triples correction is based on a perturbation theory estimate of the effect of these excitations which should be valid if MP4(DQ) and CCD correlation energies agree. Unfortunately, it is not clear that for this case the correlation energies [6] are sufficiently close to give an accurate estimate for the ^3D state when $3s3p$ correlation is included. Furthermore, the utility of this approach is limited by the fact that the method of estimating the contribution of single and triple excitations cannot be applied to the ^1S state.

Salter, Adamowicz and Bartlett (SAB) [7] consider the separations in the Ni atom using many-body perturbation theory, CCSD and CCSD+T(CCSD) methods. These CC methods more rigorously include the effect of single and triple excitations than the approach used by RM and unlike RM, the approach used by SAB seems able to treat all three states. Unfortunately it is not possible to carefully compare these results to the SDCI results. This arises since their STO basis set has sizeable (0.4 eV) errors in the separation at the SCF level relative to NHF and the GTO basis set is quite modest in size especially considering the fact that they correlated the $3s$ and $3p$ as well as the $3d$ and $4s$ electrons. Specifically, the GTO basis lacks a sufficient number of f functions to correlate 18 electrons and does not contain g functions. (Note that in the earlier SAB GTO calculations [7a] the ^3F state is contaminated with ^3P [14], but this is corrected in the SAB erratum [7b].) A comparison with the CI results is further complicated by the fact that SAB only report results correlating 18 electrons. The RM [6] calculations suggest that the problems associated with perturbation methods become more severe when the $3s$ and $3p$ electrons are correlated, and we note that the separations computed by SAB depend quite strongly on the method of determining the effect of the triple excitations. For example the $T(4)$ approximation predicts a −1.44 eV contribution to the ^3D-^1S separation while the T(CCSD) approximation predicts only −0.53 eV. Furthermore SAB note that preliminary calculations using the CCSDT-1 model lowers the total energy by 0.53 eV because the triples affect the T_2 amplitudes. Thus while these methods show some promise more work is needed.

The large differential effect of the $+Q$ correction on the ${}^3D$-${}^1S$ separation lead to the suggestion that the reference space must be improved [4], and that an MCSCF/CI approach would be more appropriate. While it is less obvious, it has also been shown that $3d$-shell radial correlation effects are important in the $3d^n4s^2$ and $3d^{n+1}4s^1$ occupations [2, 3, 15]. Dunning and co-workers [2, 3] have argued that the states arising from the $3d^{n+1}4s^1$ occupation are like O^- or F^-, that is, the $3d$ shell is best described as n electrons in a tight $3d$ orbital (like the $3d$ orbital in the $3d^n4s^2$ occupation) and an extra $3d$ electron in a diffuse $3d$ orbital. Incorporating this idea into an MCSCF calculation [2, 3] leads to a significant improvement over the SCF separations. However, the results of limited CI calculations (SCF+1+2) using these MCSCF orbitals [3] still show significant errors when compared to experiment.

In this work we report results of an extensive study of the Ni atom separations using extended Gaussian basis sets. The orbital determination is performed using a large CASSCF configuration expansion that includes $3d$ to $3d'$ excitations. Finally, large multireference CI wave functions are constructed based on these orbitals. Energetically large radial correlation effects associated with the $3d$ shell are found, particularly in the case of the $3d^{10}$ state. When these $3d \rightarrow 3d'$ excitations are included in the reference we find a substantial improvement in the $3d^94s^1$-$3d^{10}$ excitation energy, bringing this into close agreement with experiment (an error of 0.1 eV) and also an improved theoretical value for the $3d^94s^1$-$3d^84s^2$ excitation energy.

2. Methods

The Ni basis set is derived from the $(20s\,12p\,9d)$ energy optimized basis of Partridge [16] extended by three even-tempered $2p$ and one $3d$ functions. This basis is further extended to $(20s\,15p\,10d\,6f)$ by adding six $4f$ functions obtained by optimizing a single $4f$ exponent ($\alpha = 2.0$) at the SDCI level and expanding to six even-tempered functions centered around this exponent using a scale factor of 2.5 (highest exponent thus obtained is 19.7642). This primitive basis set was then generally contracted [17] using atomic natural orbitals (ANO) [18] obtained from averaged density matrices from SDCI calculations on the ${}^3F$, ${}^3D$ and ${}^1S$ states. Several successively larger ANO basis sets were constructed (Table 1) to ensure that the splittings of the uncontracted basis set were accurately reproduced. The outermost $1s$ and $2p$ functions were left uncontracted to improve the flexibility of the basis set. Using the $[7s\,6p\,4d\,2f]$ contracted basis four primitive $5g$ functions obtained as $\alpha = 0.6072 * 2.5^k$, with $k = 0, \ldots, 3$, were added and the ANO contraction process repeated for the $5g$ functions to obtain a final contracted basis set consisting of $(20s\,15p\,10d\,6f\,4g)/[7s\,6p\,4d\,3f\,2g]$. In all calculations only the true spherical harmonic components of the d, f and g functions were retained.

Table 1. Effect on the Ni atom separations (eV) of ANO basis set contraction of (20*s* 15*p* 10*d* 6*f*) primitive basis and of the contraction of the four 5*g* primitives. SCF orbitals used throughout; the results with the Davidson correction are in parentheses. The results do not contain any relativistic corrections

Basis set	SCF		SDCI	
	$3d^9 4s^1$-$3d^8 4s^2$	$3d^9 4s^1$-$3d^{10}$	$3d^9 4s^1$-$3d^8 4s^2$	$3d^9 4s^1$-$3d^{10}$
NHF[a]	−1.275	4.197		
(20*s* 15*p* 10*d* 6*f*)	−1.277	4.199	−0.070 (−0.060)	2.299 (2.080)
[7*s* 5*p* 3*d* 2*f*]	−1.279	4.202	−0.058 (−0.041)	2.266 (2.052)
[7*s* 6*p* 4*d* 2*f*]	−1.276	4.198	−0.065 (−0.057)	2.270 (2.049)
[7*s* 6*p* 4*d* 2*f*](4*g*)			+0.018 (+0.030)	2.261 (2.034)
[7*s* 6*p* 4*d* 2*f* 1*g*]			−0.010 (0.000)	2.285 (2.062)
[7*s* 6*p* 4*d* 3*f* 2*g*]			+0.020 (+0.035)	2.274 (2.051)

		Total energies (E_H)		
		$3d^8 4s^2 (^3F)$	$3d^9 4s^1 (^3D)$	$3d^{10} (^1S)$
	NHF[a]	−1506.871288	−1506.824414	−1506.670180
(20*s* 15*p* 10*d* 6*f*)	SCF	−1506.870250	−1506.823313	−1506.669000
[7*s* 6*p* 4*d* 2*f*]	SCF	−1506.870123	−1506.823228	−1506.668965
(20*s* 15*p* 10*d* 6*f*)	SDCI[b]	−1507.178854	−1507.176292	−1507.091796
[7*s* 6*p* 4*d* 2*f*]	SDCI	−1507.166885	−1507.164479	−1507.081044
[7*s* 6*p* 4*d* 2*f*](4*g*)	SDCI	−1507.187630	−1507.188282	−1507.105185
[7*s* 6*p* 4*d* 3*f* 2*g*]	SDCI	−1507.191104	−1507.191774	−1507.108189

[a] Numerical Hartree–Fock results from [19], more accurate NHF calculations from [16] yield total energies of −1506.870907 and −1506.824027 for the ^3F and ^3D states, respectively. Note that the more accurate total energies affect the separation by only 0.001 eV

[b] Ten electrons are correlated

Correlation was included either using (single-reference) SDCI and MCPF [20] wave functions based on SCF orbitals or a multireference CI (MRCI) treatment based on CASSCF [21] orbitals. The list of references for the MRCI was constructed at two different selection levels using thresholds of 0.05 and 0.01 in the coefficients obtained from a CASSCF calculation. For all three states, the $3d$ and $3d'$ orbitals were included in the active space (MC-$3d3d'$). For the $3d^8 4s^2$ occupation, because of the $4s$-$4p$ near degeneracy, the $4s$ and $4p$ orbitals were also included in the active space in some calculations, (MC-$4s4p3d3d'$). The $3d^9 4s^1$ MC-$3d3d'$ calculation also had the $4s$ orbital active, but restricted to a fixed occupation of one electron. To reduce the configuration space, the excitations were restricted to a fixed occupation for each $3d$-$3d'$ pair and no cross-excitations between pairs were allowed. For the ^1S state, this is a strongly orthogonal generalized valence bond (SOGVB) wave function [22], and one very similar in spirit for the other states. This restriction has a negligible effect (less than 0.03 eV) on the $3d^9 4s^1$-$3d^{10}$ CASSCF excitation energy. In each case full symmetry and equivalence restrictions were imposed as described in [23].

In the CI(0.05) calculations, all occupations for which any of the component configurations has a coefficient greater than 0.05 in the CASSCF wave function, described above, were selected as references. In the case of Ni $3d^8 4s^2 (^3F)$ this leads to no additional $3d$ to $3d'$ reference states, but to three additional reference states describing the $4s$–$4p$ near-degeneracy. Since no occupations involving the $3d'$ orbital were in the CI reference space, the $3d'$ orbitals were eliminated from the CASSCF active space leading to a (MC-$4s4p$) treatment for the orbital optimization. For the $3d^9 4s^1 (^3D)$ state, where the 0.05 threshold for the CI reference selection yields only the SCF occupation, the $3d'$ orbital was removed from the CASSCF space, and thus SCF orbitals were used in the CI(0.05) $3d^9 4s^1$ calculations. For Ni $3d^{10}$ the radial correlation effects in the $3d$ shell are more important and leads to 11 references at the 0.05 threshold: the appropriate orbitals in this case are clearly those from the MC-$3d3d'$ calculation.

When the selection threshold is decreased to 0.01, the number of references increases substantially in each case. The MRCI calculations on the $3d^9 4s^1$ and $3d^{10}$ states employed respectively 17 and 20 references consisting entirely of $3d \rightarrow 3d'$ excitations, and were performed using the MC-$3d3d'$ orbitals. For Ni $3d^8 4s^2$, 19 configurations above the threshold are found consisting of both $4s^2 \rightarrow 4p^2$ and $3d \rightarrow 3d'$ excitations. The large number of active orbitals in the reference space made this calculation intractable with the current programs, and the $3d^8 4s^2$ state was computed using the 16 references arising from $3d$–$3d'$ excitations and the MC-$3d3d'$ orbitals leaving out the $4s^2 \rightarrow 4p^2$ reference states. In order to help estimate the effect of neglecting the references involving $4s^2 \rightarrow 4p^2$, some calculations were performed on the $3d^6 4s^2 (^5D)$ and $3d^7 4s^1 (^5F)$ states of Fe where it is possible to include the references involving $4s^2 \rightarrow 4p^2$ and the $3d \rightarrow 3d'$ excitations simultaneously. These Fe calculations were performed in the ANO basis set used in the recent full CI study on Fe [24]. This provides a calibration of the reference selection procedures.

Relativistic effects were computed using first-order perturbation theory estimates of the Darwin and mass-velocity terms [25] in the uncontracted ($20s$ $15p$ $10d$ $6f$) basis at the SCF, SDCI and MCPF levels. The contracted basis set was found to give very unreliable estimates of the differential relativistic effects between states. The effect of correlating the $3s3p$ orbitals was investigated using the size-consistent MCPF technique, in the uncontracted basis. The CI calculations were performed using the MOLECULE-SWEDEN codes [26, 27], while the MCPF calculation used the code developed by Blomberg and Siegbahn [20].

3. Results and discussion

The ANO basis set contraction scheme combined with a vectorized integral evaluation program [26] allows for substantially larger primitive basis sets than previously, while still retaining the advantages of a compact contracted basis. The primitive GTO basis set used in the present case is large enough to reproduce the numerical Hartree-Fock total energies for all three states (Table 1) to within 0.03 eV. The contraction of the s, p and d spaces to [$7s$ $6p$ $4d$] results in negligible loss of energy at the SCF level even though the contraction is based on averaged orbitals. Using the natural orbitals as contraction coefficients also results in a minimal loss of energy at the correlated levels for each contraction and provides a systematic procedure to extend the contracted basis set [18]. The final [$7s$ $6p$ $4d$ $2f$] ANO contraction based on the averaged natural orbitals from the three different states accurately reproduces the uncontracted basis set results for the splittings at each level of theory (Table 1). The addition of four uncontracted $5g$ functions to this basis has a large effect (0.08 eV) on the $3d^9 4s^1$-$3d^8 4s^2$ separation while the $3d^9 4s^1$-$3d^{10}$ separation is much less affected (0.01 eV). The size of this effect suggests some additional improvements in the $3d^9 4s^1$-$3d^8 4s^2$ separation may still be obtained with further extensions of the basis set.

The importance of correlating the $3s3p$ orbitals has been studied previously [1, 4] with only small effects found on the excitation energies. This is also verified in the present investigation where we compute the effect on the separations using a modified version, MCPF [20], of the size-extensive CPF method [28]. The effect on the $3d^9 4s^1$ to $3d^8 4s^2$ excitation energy is found to be smaller than 0.01 eV (Table 2) while for the $3d^9 4s^1$-$3d^{10}$ separation the effect is larger, but still only 0.03 eV. The effects of including the $3s3p$ orbitals is thus found to be quite small. In the previous FCI study of Fe atom [24] it was concluded that the differential effect of $3s$ and $3p$ correlation was probably underestimated at the SDCI or SDCI+Q levels; for Fe, the true effect of the $3s$ and $3p$ correlation is probably 1.5 times that computed. However, even if the MCPF underestimates the effect of $3s$ and $3p$ correlation in Ni by a factor of two, the effect is significantly smaller than the 0.1-0.3 eV reported by Rohlfing and Martin [6] using a CCD approach.

The effect of relativity is estimated using first-order perturbation theory. At the SCF level the results agree with those of Martin and Hay [10] who included the mass-velocity and Darwin terms in their numerical Hartree-Fock treatment. The relativistic effects are essentially unaffected by correlation with a decrease of only 0.02-0.03 eV obtained from a correlation treatment which includes the

Table 2. Effects of relativity and $3s3p$ correlation on the Ni excitation energies (eV) using the uncontracted ($20s$ $15p$ $10d$ $6f$) basis

Method	$3d^9 4s^1$-$3d^8 4s^2$			$3d^9 4s^1$-$3d^{10}$		
	Non-rel	Rel	Δ[a]	Non-rel	Rel	Δ[a]
SCF	−1.277	−1.637	−0.360	4.199	4.404	0.205
SDCI(10)[b]	−0.070	−0.436	−0.366	2.299	2.512	0.213
MCPF(10)[c]	−0.085	−0.446	−0.361	2.035	2.259	0.224
MCPF(18)[d]	−0.077	−0.408	−0.331	2.064	2.268	0.204

[a] Relativistic contribution to excitation energy

[b] The number of electrons correlated is given in parentheses

[c] The total energies are −1507.200987, −1507.197876 and −1507.123100 E_H for the ^3F, ^3D and ^1S states, respectively

[d] The total energies are −1507.563364, −1507.560526, and −1507.484679 E_H for the ^3F, ^3D and ^1S states, respectively

$3s3p$ orbitals. Thus we find essentially no coupling between correlation and relativity.

The results from our more extended treatments using the [$7s\,6p\,4d\,3f\,2g$] basis set are given in Table 3. Focusing first on the $3d^94s^1$-$3d^{10}$ excitation energy, the effects of successive improvements in the correlation treatment will be studied. At the SDCI level the excitation energy is 2.48 eV compared to the experimental excitation energy of 1.74 eV. As noted previously [1, 4] there is a sizeable differential effect of higher excitations as estimated using the Davidson correction. This results in a decrease in the excitation energy of 0.2 eV. When the $3d \rightarrow 3d'$ excitations are added to the CASSCF active space a very large effect (7 eV) on the ^1S total energy is obtained. As no configurations with coefficients above 0.05

Table 3. Computed excitation energies (eV) for Ni atom using [$7s\,6p\,4d\,3f\,2g$] basis set and different levels of correlation treatment. Values in parentheses have $3s3p$ correlation added in from Table 2. We have added a relativistic correction based on the NHF calculations of Martin and Hay [10] (see text)

	SDCI and MCPF				
	SCF	MCPF	CI	CI+Q	Ref.[a]
$3d^84s^2$(SCF)	−1.636	−0.355	−0.340	−0.325	1
$3d^94s^1$ (SCF)	0.000	0.000	0.000	0.000	1
$3d^{10}$ (SCF)	4.408	2.239	2.484	2.261	1
	CI(0.05)				
	SCF/MCSCF	CI	CI+Q	Ref.	
$3d^84s^2$ (MC-$4s4p$)[b]	−2.471	−0.633	−0.444	4	
$3d^94s^1$ (SCF)	0.000	0.000	0.000	1	
$3d^{10}$ (MC-$3d3d'$)[c]	−2.639	1.304	1.525	11	
	CI(0.01)[d]				
	MCSCF	CI	CI+Q	Ref.	
$3d^84s^2$ (MC-$4s4p3d3d'$)[e]	−0.934				
$3d^84s^2$ (MC-$3d3d'$)	−0.096	−0.086 (−0.078)	−0.195 (−0.187)	16	
$3d^94s^1$ (MC-$3d3d'$)	0.000	0.000 (0.000)	0.000 (0.000)	17	
$3d^{10}$ (MC-$3d3d'$)	2.330	1.879 (1.908)	1.843 (1.872)	20	
	Expt.[f]				
$3d^84s^2$	0.03				
$3d^94s^1$	0.00				
$3d^{10}$	1.74				

[a] Number of configurations in reference space

[b] Active space containing $4s$ and $4p$ orbitals

[c] Active space ccontaining $3d$ and $3d'$ orbitals

[d] The total MRCI energies are −1507.208402, −1507.218106, and −1507.156756 E_H for the ^3F, ^3D and ^1S states, respectively

[e] Active space containing $3d$, $3d'$, $4s$ and $4p$ orbitals

[f] Experimental values (J-averaged) from [9]

are found for the $3d^9 4s^1$ state in the CASSCF wave function, the SCF treatment is appropriate for this state at this level of approximation. Correlation included through a single-reference SDCI on the $3d^9 4s^1$ state and an 11-reference MRCI on the $3d^{10}$ state, CI(0.05), yields a $3d^9 4s^1$-$3d^{10}$ excitation energy of 1.30 eV. However, an indication of missing references in the description of $3d^9 4s^1$ is obtained from the Davidson estimate of higher excitations. In this case the differential effect of the Davidson correction is of the same size (0.22 eV) as in the single-reference SDCI, but of the opposite sign, increasing the excitation energy from 1.30 eV to 1.53 eV. Improving the reference space to include all CASSCF configurations with coefficients greater than 0.01 gives 17 and 20 references for the $3d^9 4s^1$ and $3d^{10}$ states, respectively, and results in an excitation energy of 1.88 eV in good agreement with the experimental value, 1.74 eV. In this case no indication of missing differential effects of higher excitations is given by the Davidson correction. Thus a proper description of the radial correlation effects associated with the $3d$ shell is a prerequisite for an accurate determination of the $3d^9 4s^1$-$3d^{10}$ excitation energy.

Turning now to the $3d^9 4s^1$-$3d^8 4s^2$ excitation energy the SDCI result is −0.34 eV, compared with the experimental value of 0.03 eV. In this case no large differential effects of higher excitations are indicated through the Davidson correction. However, in the case of the Ni $3d^8 4s^2$ state the $4s$-$4p$ near-degeneracy results in a large decrease in the coefficient, C_0, of the reference occupation in the SDCI wave function, which is used to scale the correlation energy. As the change in C_0 is not related to the large correlation energy obtained from correlating the $3d$ electrons, the Davidson estimate becomes particularly unreliable and is probably an over-estimate for the $3d^8 4s^2$ state [24].

Including the $4s$-$4p$ orbitals in the orbital determination (MC-$4s4p$) leads to an energy lowering of the $3d^8 4s^2$ state of 0.84 eV over the SCF result. Using these orbitals and including the three additional reference configurations in the CI, CI(0.05), yields −0.63 eV, with a large Davidson correction that favors the $3d^9 4s^1$ state. Including the $3d$, $3d'$, $4s$ and $4p$ orbitals in the active space for $3d^8 4s^2$ leads to a CASSCF excitation energy of −0.93 eV to be compared with the value of −2.47 eV obtained when only the $4s$-$4p$ near-degeneracy effect is taken into account. The corresponding CI(0.01) calculation would thus require 17 and 19 configurations respectively for $3d^9 4s^1$ and $3d^8 4s^2$. However, including the $4p$ orbitals in the reference space unfortunately results in a greater number of active orbitals than is possible to treat with the present algorithms to generate the symbolic formula tape. The CI(0.01) was thus performed without these $4s^2 \rightarrow 4p^2$ references, and instead we will attempt to estimate their effect on the excitation energy based on comparisons with the Fe atom calculations.

The CI(0.01) results in a $3d^9 4s^1$-$3d^8 4s^2$ separation of −0.09 eV in good agreement with the experimental value of 0.03 eV. However, it must be recalled that for the $3d^8 4s^2 (^3F)$ state the $4s^2 \rightarrow 4p^2$ references were not included. One estimate of the effect of these missing references is obtained from the difference in the computed separation between the SCF/SDCI treatment and the result where the $4s^2 \rightarrow 4p^2$

references are included, the CI(0.05) calculations in Table 3. We find a large (0.29 eV) differential effect from including these references. This is clearly an overestimation of the effect on the CI(0.01) result, which can be understood by the following simple argument. If in the CI(0.01) treatment, the $3d$-$3d'$ reference states gave all the $3d$ correlation energy, the subsequent MRCI calculation would have to recover only the $4s$ correlation. As the $4s$ correlation is a two electron problem, the energy would be independent of using only the $4s^2$ reference or including the $4s^2 \rightarrow 4p^2$ reference states as well. The correct effect of the $4s$-$4p$ reference states is therefore somewhere between zero and 0.29 eV. Another estimate of the effect of the missing references in the CI(0.01) calculation is of course also provided by the Davidson correction, which in this case is 0.11 eV.

The correlation energy associated with the $4s$-$4p$ near-degeneracy in the $3d^6 4s^2(^5D)$ state of Fe is similar to that in the ^3F state of Ni. Also the $3d$-$3d'$ correlation energy in Fe is very large, and it has a large differential effect on the ^5D-$^5F(3d^7 4s^1)$ separation, as it does for the Ni ^3D-^3F separation. Therefore we use this Fe atom separation to calibrate a method of estimating the actual effect of $4s^2 \rightarrow 4p^2$ reference states on the CI(0.01) calculation in Ni. For the Fe separations it is possible to perform the MC-$4s4p3d3d'$/CI(0.01) calculation. In addition, recently published results [24] of full CI (FCI) calculations on this atomic separation using a $(14s\ 11p\ 6d\ 3f)/[5s\ 4p\ 2d\ 1f]$ ANO basis are available for comparison. Our results for this separation using the same ANO basis as in [24] and the different levels of correlation defined above are given in Table 4.

The first important information from the Fe atom calculations is that the CI(0.01) calculation also including the $4s$-$4p$ reference states gives a separation in close agreement with full CI. Second, for Fe the effect of adding the $4s$-$4p$ reference states goes down from 0.20 eV in the CI(0.05) case, to 0.10 eV in the CI(0.01) case. The Fe atom results also show that the Davidson correction at the CI(0.01) level of 0.13 eV is an overestimate of the actual effect of missing $4s^2 \rightarrow 4p^2$ references (0.09 eV). As the Davidson correction in the MC-$3d3d'$/CI(0.01) calculation on Fe(^{5}D) overestimates the importance of the $4s$-$4p$ near degeneracy by 44%, it seems that an upper bound to this effect in Ni would then be the full Davidson correction. This yields a ^3D-^3F separation which is in error by 0.23 eV. This is about twice the error in the $3d^9 4s^1 \rightarrow 3d^{10}$ excitation. However there is probably no single large effect missing in our ^3D-^3F calculations. In this regard, if one assumes that the Davidson correction overestimates the $4s$-$4p$ near degeneracy effect in Ni by the same percent as in Fe, the error would be reduced by 0.03 eV. If instead of using the relativistic correction based upon the NHF wave functions, we use the value computed at the MCPF level correlating the $3s$ and $3p$ electrons, the error is reduced by an additional 0.03 eV. The 0.08 eV differential effect of adding g functions suggest some remaining basis set effects. Based on the Fe FCI calculations, $3s$ and $3p$ correlation, which reduces the error in the Ni ^3D-^3F separation by only 0.01 eV at the MCPF level, may be somewhat of an underestimate. Since all of these small errors work in the same direction, eliminating the remaining 0.23 eV error is expected to require significantly larger calculations than those reported in this work.

Table 4. Results for Fe atom $3d^6 4s^2(^5D)$-$3d^7 4s^1(^5F)$ separations (eV) correlating 8 electrons at different levels of CI treatment. Percent correlation energy recovered compared with FCI given in parentheses

	SCF/MCSCF	CI	CI+Q
SDCI			
$3d^6 4s^2$ (SCF)	0.000	0.000 (92.5)	0.000 (99.0)
$3d^7 4s^1$ (SCF)	1.858	1.191 (93.6)	1.259 (98.0)
CI(0.05)			
$3d^6 4s^2$ (MC-$4s4p$)[a]	0.000	0.000 (96.8)	0.000 (99.9)
$3d^7 4s^1$ (SCF)	2.674	1.393 (93.6)	1.301 (98.0)
CI(0.01)[b]			
$3d^6 4s^2$ (MC-$3d3d'$)[c]	0.000	0.000 (96.7)	0.000 (100.8)
$3d^7 4s^1$ (MC-$3d3d'$)	0.572	1.110 (98.8)	1.239 (100.0)
CI(0.01)[d]			
$3d^6 4s^2$ (MC-$4s4p3d3d'$)[e]	0.000	0.000 (99.0)	0.000 (100.2)
$3d^7 4s^1$ (MC-$3d3d'$)	1.390	1.216 (98.8)	1.211 (100.0)
FCI[f]	—	1.202	—

[a] Active space containing $4s$ and $4p$ orbitals
[b] $4s^2 \rightarrow 4p^2$ references not included
[c] Active space containing $3d$ and $3d'$ orbitals
[d] $4s^2 \rightarrow 4p^2$ references included
[e] Active space containing $4s$, $4p$, $3d$ and $3d'$ orbitals
[f] Full CI result from [24]

Perhaps the most interesting aspect of the present calculations is the large difference between the results of the multireference CI and the single-reference-based methods, particularly for the $3d^9 4s^1 \rightarrow 3d^{10}$ excitation. This is a rather surprising result since only the reference configuration has a coefficient with absolute value larger than 0.05 in the single-reference CI wave function. The non-negligible effect of 0.2 eV on the splitting from the Davidsons's correction has, however, also been noted before [4]. It should be observed that the poor splitting obtained with one reference state, with an error of more than 0.5 eV, is present irrespective of which particular single reference method is used: SDCI + Q, MCPF, CEPA-1 [5] or CCSD [6, 7] all give the same poor splitting. This splitting is otherwise a case where different treatments of unlinked quadruples might have been critical. The basis of the MCPF and CEPA-1 methods is that they essentially agree with the full CCSD method for independent electron pairs (this is approximately true for the Davidson correction when 8–12 electrons are correlated), but the case of the nickel $3d$ shell is far from this idealized situation. Nevertheless, the agreement between the methods is surprisingly close. From the results in [6, 7], if coupled-cluster-based methods with only one reference state are to be used to calculate the splittings in the nickel atom, the critical point is an accurate inclusion of linked triples; MBPT at fourth order is far from sufficient for this purpose. Clearly it would be very useful to have calculations similar to those reported [7] by SAB performed correlating both 10 and 18 electrons in a large basis set. This would allow a critical comparison of the CCSD+T and CASSCF/MRCI methods.

4. Conclusions

The splittings between the lowest ^3D, ^3F and ^1S states of nickel atom have been calculated with MRCI methods and using large ANO basis sets. The most significant improvement compared to earlier calculations is that the error for the ^3D-^1S excitation is reduced to 0.14 eV. With addition of the Davidson correction the result is actually within 0.1 eV of the experimental result. The best previous calculations had errors of at least 0.5 eV for this excitation energy. The main reason for the significant improvement is that we have incorporated $3d$-$3d'$ configurations in the zeroth-order treatment. The most important $3d$-$3d'$ configurations were selected as reference states in the MRCI calculations from a preceding 10 electron CASSCF calculation. The importance of $3d$-$3d'$ radial correlation shows up already in the CASSCF results which represent significant improvements for the atomic splittings compared to the SCF results; a similar improvement in the $3d^{n+1}4s^1$-$3d^{n+2}$ separation with the inclusion of the $3d$-$3d'$ radial correlation has been found for other transition metal atoms [3]. Also the ^3D-^3F splitting is improved in the present calculations, although not as significantly. The best MRCI value, including an estimate for the effect of higher excitations, is 0.23 eV away from the experimental value. The indications are that higher angular momentum functions than g may be of non-negligible importance for this excitation.

References

1. Martin RL (1980) Chem Phys Lett 75:290
2. Dunning TH, Botch BH, Harrison JF (1980) J Chem Phys 72:3419
3. Botch BH, Dunning TH, Harrison JF (1981) J Chem Phys 75:3466
4. Bauschlicher CW, Walch SP, Partridge H (1982) J Chem Phys 76:1033
5. Werner HJ (1984) Faraday Symp Chem Soc 19:202
6. Rohlfing CM, Martin RL (1985) Chem Phys Lett 115:104
7. (a) Salter EA, Adamowicz L, Bartlett RJ (1985) Chem Phys Lett 122:23; also see erratum, (b) Salter EA, Adamowicz L, Bartlett RJ (1986) Chem Phys Lett 130:152
8. Langhoff SR, Bauschlicher CW (1986) J Chem Phys 84:4485
9. Moore CE (1949) Atomic energy levels. Natl Bur Stand (US) 467
10. Martin RL, Hay PJ (1981) J Chem Phys 75:4539
11. Walch SP, Bauschlicher CW, Langhoff SR (1985) J Chem Phys 83:5351
12. Gray JA, Rice SF, Field RW (1985) J Chem Phys 82:4717
13. Langhoff SR, Davidson ER (1974) Int J Quantum Chem 8:61; Davidson ER (1984) In: Daudel R, Pullman B (eds) The world of quantum chemistry. Reidel, Dordrecht
14. Rohlfing CM (1986) Chem Phys Lett 127:183
15. Froese-Fischer C (1977) J Phys B10:1241
16. Partridge H, to be published
17. Raffenetti RC (1973) J Chem Phys 58:4452
18. Almlöf J, Taylor PR (1987) J Chem Phys 86:4070
19. Hay PJ (1977) J Chem Phys 66:4377
20. Chong DP, Langhoff SR (1986) J Chem Phys 84:5606. The direct-CI MCPF program was written by Blomberg MRA, Siegbahn P

21. Siegbahn PEM, Heiberg A, Roos BO, Levy B (1980) Physica Scripta 21:323; Roos BO, Taylor PR, Siegbahn PEM (1980) Chem Phys 48:157; Siegbahn PEM, Almlöf J, Heiberg A, Roos BO (1981) J Chem Phys 74:2381
22. Dunning TH (1984) In: Dykstra CE (ed) Advanced theories and computational approaches to the electronic structure of molecules. Reidel, Dordrecht
23. Bauschlicher CW, Taylor PR (1988) Theor Chim Acta 74:63–73
24. Bauschlicher CW (1987) J Chem Phys 86:5591
25. Martin RL (1983) J Phys Chem 87:750; see also Cowan RD, Griffin DC (1976) J Opt Soc Am 66:1010
26. MOLECULE is a vectorized Gaussian integral program written by Almlöf J
27. SWEDEN is a vectorized SCF-MCSCF-direct CI- conventional CI-CPF-MCPF program, written by Siegbahn PEM, Bauschlicher Jr CW, Roos B, Taylor PR, Heiberg A, Almlöf J, Langhoff SR, Chong DP
28. Ahlrichs R, Scharf P, Jankowski K (1985) J Chem Phys 82:1413

Note added in proof. After this manuscript was accepted for publication a new symbolic formula generation program was written by one of us (PS) which has allowed us to perform the $3d^8 4s^2$ (MC-$4s4p3d3d'$)CI(0.01) calculation. This yields a ^3F–^3D separation of −0.289 eV at the CI level and −0.237 eV with the addition of the $+Q$ correction, or an error of 0.32 and 0.27 eV. This is somewhat larger than our estimate of a 0.23 eV error based on the Fe results.