

Relativistic calculations on the adsorption of CO on the (111) surfaces of Ni, Pd, and Pt within the zeroth-order regular approximation

P. H. T. Philipsen, E. van Lenthe, J. G. Snijders, and E. J. Baerends

Department of Theoretical Chemistry, Vrije Universiteit, De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands

(Received 27 June 1997)

In this paper we first describe the implementation of the zeroth-order regular approximation (ZORA) for relativistic effects in our density-functional program for extended systems. The ZORA formalism affords approximations, which are discussed and tested, that reduce the computational effort of scalar relativistic calculations to that of nonrelativistic calculations, the inclusion of spin-orbit coupling requiring additional effort. Second, we present the outcome of nonrelativistic, scalar relativistic, and spin-orbit coupling calculations on the adsorption energy of CO on the (111) surfaces of Ni, Pd, and Pt. Relativity has a modest effect for CO on Pd, but proves to be essential for CO on Pt. The relativistic correction for the CO/Pt adsorption energy is as large as 70% at the scalar relativistic level and 55% when including spin-orbit coupling. In addition, relativity changes the preferred adsorption site for CO/Pt from hollow to top. We have examined the effects of spin polarization and of different exchange-correlation functionals, i.e., the local-density approximation (LDA) versus two generalized gradient approximations (GGA). The GGA's correct the severe overbinding by LDA of CO to the metal surfaces, and yield good agreement with experiment for adsorption energies and sites. [S0163-1829(97)04740-1]

I. INTRODUCTION

Relativity is known to be of utmost importance for compounds containing elements from the sixth and seventh period. In density-functional theory mostly the Dirac-Slater equation is taken as a starting point, with Slater's original exchange functional replaced by expressions resulting from for instance the local-density approximation (LDA) or a generalized gradient approximation (GGA). Since this equation is usually too time consuming to solve, approximations have to be made in practice. The first-order relativistic terms (Pauli) in the Hamiltonian may be used in a coupled perturbative scheme,¹⁻³ while certain higher-order effects may be incorporated by diagonalization of the Pauli Hamiltonian in a restricted space.^{4,5} The two-component approximate relativistic Hamiltonian resulting from the Douglas-Kroll-Hess transformation is widely used, see, for example, Ref. 6 and references therein, as is of course the pseudopotential approximation.⁷ Recently it has been shown that two-component relativistic Hamiltonians can be derived that are regular at the Coulombic singularities in the potential at the nuclear positions.⁸ The zeroth-order regular approximation (ZORA) constitutes an efficient tool to calculate bonding energies of molecules, with results that are practically identical to full Dirac energies.⁹ Since the ZORA Hamiltonian is bounded from below,¹⁰ standard variational techniques can be used to do fully self-consistent calculations.

The relativistic effect has been the subject of many studies on molecules¹¹⁻¹⁴ and solids.^{15,16} As for slabs Szunyogh and co-workers¹⁷ have studied the density of states for Pt and Au surfaces with a fully relativistic screened Korrington-Kohn-Rostoker (SKKR) Green-function method. With a similar Green-function tight-binding linear-muffin-tin-orbital (TB-LMTO) method the properties of random alloy surfaces have been studied.¹⁸ In both the SKKR and TB-LMTO calcula-

tions use is made of the atomic sphere approximation, which is a restriction on the potential. We are not aware of a study of the relativistic effect, including spin-orbit coupling, on molecule-surface interactions.

We will in this paper discuss the implementation of the ZORA method in our band-structure program, with special emphasis on further approximations that will make the relativistic calculations highly efficient. Since the study of molecule-surface interactions is the primary purpose (cf. Refs. 20 and 21) we apply the method to a study of relativistic effects on the adsorption of CO on the (111) faces of Ni, Pd, and Pt. The adsorption of carbon monoxide on group-VIII metals ranks highly among the systems best studied in surface science. Several theoretical interpretations have been developed as for instance the old Blyholder²² picture of donation from the CO 5σ orbital to the metal and backdonation of the metal to the 2π orbital. A more quantitative model has been developed by Hammer, Morikawa, and Nørskov,²³ in which also the role of the metal d and sp bands is incorporated. In the field of heterogeneous catalysis transition metals serve frequently as catalysts, as, for instance, in the production of CO and H₂ through steam reforming. The resulting synthesis gas can, for instance, be used for Fischer-Tropsch synthesis. In this work we compare systematically several theoretical models for the adsorption of CO on the (111) faces of Ni, Pd, and Pt. Exposure of CO to these surfaces gives rise to a nicely ordered overlayer of chemisorbed molecules in a $\sqrt{3} \times \sqrt{3} R30^\circ$ structure, but, interestingly, the preferred adsorption site is different on these three surfaces.²⁴ In similar molecular studies on the monocarbonyls¹³ and binary carbonyls¹⁴ of Ni, Pd, and Pt, it has been shown that relativity changes the trend in bond strength and bond lengths in this series.

II. METHOD

In our band-structure program (BAND),¹⁹ part of the Amsterdam density-functional (ADF) package, the eigen-

states of the one-electron Hamiltonian are approximated by linear combinations of atomic orbitals, where both atomic solutions by numerical integration of the radial differential equation [numerical atomic orbitals (NAO's)] and Slater-type orbitals (STO's) are usually employed as basis functions. The basis set is symmetry adapted for the periodicity of the Bravais lattice by Bloch summations. For a certain point in reciprocal space the eigenstates are found by diagonalizing the corresponding Hamiltonian matrix. A constant part of this matrix is the kinetic energy matrix with elements that are, due to Bloch summations, linear combinations of the following fundamental matrix elements:

$$\langle \phi_i | T | \phi_j \rangle. \quad (1)$$

The integral is over the unit cell, but the atoms on which the atomic functions ϕ_i and ϕ_j are centered can be outside the unit cell.

The ZORA Hamiltonian differs from the nonrelativistic Hamiltonian in that the kinetic-energy operator has been replaced with

$$T^{\text{ZORA}} = \vec{\sigma} \cdot \vec{p} \frac{c^2}{2c^2 - V} \vec{\sigma} \cdot \vec{p}, \quad (2)$$

with $\vec{\sigma}$ the Pauli spin matrices. It is possible to split this operator into a spin-orbit term (regularized at the origin) and a remaining scalar relativistic part.²⁵ The scalar relativistic (SR) approximation is characterized by a ‘‘kinetic-energy’’ operator that no longer contains the Pauli spin matrices:

$$T^{\text{SR}} = \vec{p} \frac{c^2}{2c^2 - V} \vec{p}. \quad (3)$$

For convenience we will refer to this operator simply as the kinetic-energy operator T , although it does contain, in a regularized form, potential dependent relativistic corrections. The fact that this operator depends on the potential, $T = T[V]$, rather than on $E - V$ makes the total energy dependent on the gauge of the potential. Such a dependence is of course especially worrisome in bulk calculations, since there is no outer region where the potential can be required to go to zero. Fortunately, the gauge dependence can almost exactly be removed by a scaling of the orbital energies (cf. the scaled-ZORA method⁹). When only bond energies are required, i.e., energy differences between the full system and its constituents (atoms or larger fragments such as molecule and slab), it has been shown by Ref. 9 that the scaled-ZORA method leads to a particularly simple computational procedure. Within a plausible approximation for the one-electron energies of the core orbitals, called the electrostatic shift approximation (ESA), the scaled-ZORA method leads to an expression for the difference in ‘‘kinetic’’ energies of the converged final system (molecule, slab, etc.) and the constituting atoms in which only the converged molecular potential V_M features in the matrix elements of T . A very good approximation to full Dirac results is obtained in this way.⁹ The evaluation of the matrix elements of the ‘‘kinetic’’-energy operator can be done using the derivatives of the basis functions. Scalar relativistic matrix elements can, for instance, be calculated as

$$\langle \phi_i | T[V_M] | \phi_j \rangle = \sum_k \left\langle \frac{\partial \phi_i}{\partial x_k} \left| \frac{c^2}{2c^2 - V_M} \right| \frac{\partial \phi_j}{\partial x_k} \right\rangle, \quad (4)$$

which can easily be evaluated with an accurate three-dimensional numerical integration method.²⁶

We have observed that the representation of the Coulomb potential due to the valence electrons in V_M in the operator T is not very critical, the effects coming primarily from the nuclear Coulomb potentials and to a smaller but non-negligible extent from the electronic core densities. We are therefore motivated, for the sake of efficiency, to investigate approximations to (the valence part of) V_M . We will first approximate the molecular potential by the sum of the potentials of the spherical reference atoms V_{SA} , in what will be called the sum of atoms potential approximation (SAPA): $V_M \approx V_{\text{SA}}$. As a consequence, the ‘‘kinetic-energy’’ matrices, one for each k point, need to be calculated only once, exactly as in a nonrelativistic calculation, and not in every cycle of the self-consistent-field procedure. Since we use one-center basis functions we can make a further approximation,

$$T[V_{\text{SA}}] \phi_i^A \approx T[V_A] \phi_i^A, \quad (5)$$

replacing V_{SA} for a basis function on atom A by the potential of that atom, V_A , in what we will call the atomic potential approximation (APA). Our reference atoms being spherical, the action of the kinetic-energy operator on a one-center function simplifies to

$$\begin{aligned} T[V_A] \phi_i^A &= -\frac{dV_A}{dr} \frac{c^2}{(2c^2 - V_A)^2} \frac{\partial \phi_i^A}{\partial r} - \frac{c^2}{2c^2 - V_A} \nabla^2 \phi_i^A \\ &+ \frac{c^2}{(2c^2 - V_A)^2} \frac{dV_A}{dr} \frac{1}{r} \vec{l} \cdot \vec{\sigma} \phi_i^A \end{aligned} \quad (6)$$

and the last term vanishes in the scalar relativistic case. Because in spherical coordinates $\nabla^2 = (1/r)(\partial^2/\partial r^2)r - (l^2/r^2)$, there are two angular operators, l^2 and $\vec{l} \cdot \vec{\sigma}$, in Eq. (6). In the fully relativistic case we can choose the angular part of the one-center functions to be eigenfunctions of these two operators, such that only the radial part of the function is affected by the action of the operator T . In the scalar relativistic and nonrelativistic cases it suffices that the one-center functions be eigenfunctions of l^2 . The advantage of the APA over the SAPA is that instead of having to calculate the gradient of each basis function, which has three components, only the action of the scalar operator T on ϕ is needed. Since hermiticity is no longer guaranteed in the APA we restore this property by taking the average,

$$T_{ij}^{\text{APA}} = \frac{1}{2} (\langle \phi_i^A | T[V_B] \phi_j^B \rangle + \langle T[V_A] \phi_i^A | \phi_j^B \rangle). \quad (7)$$

In Table I the results of APA and SAPA for the energies of a series of diatomics are shown, and the largest difference between the two methods is 0.0004 eV. Clearly the APA is a very accurate approximation to the SAPA. These all-electron calculations have been carried out with high accuracy for the numerical integration and a large basis set consisting of one NAO plus two STO's (‘‘triple ζ ’’ quality) with polarization functions up to $l=3$ (cf. the basis for the CO on Ni, Pd, and Pt calculations as given in Table II). We have also included

TABLE I. Energy (eV) of nine diatomic compounds with respect to spherical spin-restricted reference atoms, within three approximations to the scalar relativistic version of the scaled ZORA method with exchange and correlation according to the LDA. The ESA, SAPA, and APA results are from all electron calculations. Frozen core (FC) results are presented in the column APA/FC, where for O and F the $1s$ was kept frozen, for I and Te orbitals up to $4p$ were kept frozen, and for Tl, Pb, and Bi levels up to $5p$ were frozen. The last three columns contain, in obvious notation, some differences.

	ESA ^a	SAPA	APA	APA/FC	$\Delta_{\text{ESA-SAPA}}$	$\Delta_{\text{APA-SAPA}}$	$\Delta_{\text{APA-APA/FC}}$
TlI	4.41	4.3850	4.3848	4.3843	0.03	-0.0002	0.0005
PbO	8.72	8.7002	8.6998	8.6992	0.02	-0.0004	0.0006
PbTe	5.91	5.8864	5.8864	5.8856	0.02	0.0000	0.0008
I ₂	2.96	2.9403	2.9405	2.9389	0.02	0.0002	0.0016
Bi ₂	6.00	5.9723	5.9721	5.9717	0.03	-0.0002	0.0004
HI	4.96	4.9333	4.9334	4.9327	0.03	0.0001	0.0007
TIH	3.97	3.9409	3.9408	3.9395	0.03	-0.0001	0.0013
IF	4.75	4.7270	4.7269	4.7226	0.03	-0.0001	0.0043
TIF	6.83	6.8114	6.8110	6.8092	0.02	-0.0004	0.0018

^aReference 25.

full scaled-ZORA ESA results which have been obtained²⁵ with a different program, the molecular ADF code ADF-MOL, but with an all-STO basis set of similar quality. The fact that all these energies are ~ 0.03 eV more binding than our SAPA results is probably not caused by the SAPA approximation, but should be attributed to fact that the use of a NAO, which is the exact solution in the atom, implies that we have no basis set error in the reference atoms, whereas the ADF-MOL results have a basis set error in both molecule and reference atoms, which leads to some cancellation of errors. By further enlarging the basis sets for I and Bi we have been able to reproduce the scaled-ZORA ESA results for the dimers of these atoms. We have also calculated the difference between the SAPA and APA for the solid state of Au, and even in this difficult case the error was only 0.01 eV. We conclude that the APA is a good approximation and it should provide us with binding energies that are very close to true Dirac results. With the present scheme, scalar relativistic calculations are no more expensive than nonrelativistic calculations.

We have also tested the frozen-core approximation. In our program the Hamiltonian matrix elements are evaluated by numerical integration²⁶ and all functions are represented by

the complex function values in the grid points. When spin-orbit coupling is included, they are two component. Usually a number of the atomic core orbitals that are numerical solutions of the spherical reference atoms are taken over unmodified from the atom and the valence functions are core orthogonalized by projecting out these core functions. This prevents the cores from polarizing in the molecular field, which may affect the energy directly, and also might have a slight effect on the ZORA “kinetic”-energy operator since it depends on the molecular potential. In the APA there will not be any effect, as the molecular potential is replaced by the atomic potential anyway, as far as the kinetic energy is concerned. In Table I we see that, with the choice of frozen core indicated, the frozen-core calculations almost perfectly match the all electron results, the error is at most 0.0043 eV.

Practical implementation of the ZORA formalism amounts to modification of the kinetic-energy operator. In this work we compare three different models for this operator: nonrelativistic (NR), SR, and “fully” relativistic (FR), including spin-orbit coupling. (Of course, even at the FR level relativistic effects are included only in the zero-order regular approximation.) With the relativistic effect on a property we mean the FR minus the NR value obtained for that

TABLE II. The basis is a mixture of numerical atomic orbitals and Slater-type orbitals. The numerical atomic orbitals as well as the frozen-core orbitals depend on the atomic configuration used in the numerical spherical atomic program. The configuration is specified in the second column. The third column lists the basis functions, a numerical atomic orbital indicated as NAO and a Slater orbital by its exponent. Orbitals not indicated were kept frozen.

Element	Configuration	Basis
C	s^2p^2	$2s(\text{NAO},4.60,1.28)$, $2p(\text{NAO},2.94,0.82)$, $3d(2.20)$, $4f(3.30)$
O	s^2p^4	$2s(\text{NAO},7.58,1.72)$, $2p(\text{NAO},4.08,1.12)$, $3d(2.00)$, $4f(3.00)$
Ni	d^9s^1	$3d(\text{NAO},7.00,1.54)$, $4s(\text{NAO},2.50,0.95)$, $4p(2.00,1.00)$, $4f(1.50)$
Pd	$d^{10}s^0$	$4d(\text{NAO},4.45,1.15)$, $5s(\text{NAO},2.30,0.80)$, $5p(2.00,1.00)$, $4f(1.45)$
Pt	d^9s^1	$5d(\text{NAO},4.95,1.65)$, $6s(\text{NAO},2.65,1.10)$, $6p(2.50,1.25)$, $5f(2.00)$

TABLE III. Distances (bohr) of the CO molecule to the surfaces that were used in the calculations of top, bridge, and hollow site adsorption. A distinction is made between relativistic (Rel.) and nonrelativistic (NR) calculations. The CO molecule is placed with the axis perpendicular to the surface, with the carbon atom pointing to the surface, and the distances are with reference to the carbon atom. The hollow site is the hcp hollow site, and the molecules are placed in the $(\sqrt{3}\times\sqrt{3})R30^\circ$ structure, and the C-O distance was fixed to 2.15 bohr.

	Top		Bridge		Hollow	
	Rel.	NR	Rel.	NR	Rel.	NR
CO on Ni	3.4	3.4	2.8	2.8	2.6	2.6
CO on Pd	3.6	3.6			2.8	2.8
CO on Pt	3.6	3.8			2.8	3.0

property, and with the spin-orbit effect we mean the FR minus the SR result. Each of these three models can be combined with either the spin-restricted (R), or with the spin-unrestricted (U) exchange correlation functional, and differences thus found will be called the spin-polarization effect.

The inclusion of spin polarization is done as follows. The exchange-correlation (XC) energy functionals can be expressed in terms of the density and the spin polarization ζ , that may be defined as²⁷

$$\zeta = |\text{Tr } \vec{\sigma}\rho|/\rho, \quad (8)$$

with ρ the 2×2 spin-density matrix. In the absence of spin-orbit coupling the direction of the spin polarization is arbitrary, and it can be chosen to be along the z axis, in which case ζ is found by

$$\zeta = (\rho_{\alpha\alpha} - \rho_{\beta\beta})/\rho. \quad (9)$$

In all calculations we have used the latter expression for ζ , which is correct in the nonrelativistic limit, but is an approximation for the spin-orbit calculations on heavy systems.

III. COMPUTATIONAL DETAILS

We have taken two unreconstructed metal layers to model the substrate. As reconstruction is usually small for close-packed (111) surfaces, and earlier studies of convergence with number of layers have demonstrated that two-layer calculations produce realistic geometries and adsorption energies,^{28,29} these substrates are a reasonable model for the study of the relativistic effect. A description of the basis sets can be found in Table II. The C and O basis sets consisted of one NAO augmented with two STO's for the $2s$ and $2p$ orbitals and one polarization function with $l=2$. The transition metals had one NAO plus two STO's for the $(n-1)d$ and ns orbitals and two np functions. It has been shown that the basis set error of such a "triple ζ " basis set for the first bond dissociation energy of $\text{Cr}(\text{CO})_6$ is only a few hundredths of an eV.³⁰ We have tested the effect of adding f functions to the basis set by doing scalar relativistic calculations with CO at the preferred adsorption sites on Ni, Pd, and Pt. The adsorption energy was affected less than 0.1 eV, and therefore we have found it reasonable to remove the f functions from the basis sets. As for the integration over the

Brillouin zone (BZ) we have first used six symmetry-unique points in the irreducible wedge. Increasing that number to 15 changed the energy of the clean Pt slab by 0.4 eV. We have repeated all calculations for CO on Pt with 15 k points and the largest change in adsorption energies such found was 0.15 eV. Once more doubling the number of k points changed the total energy of the clean slab by only 0.03 eV. Since the effect on the adsorption energies will probably be even less, we can consider the calculation with 15 k points, as we have used in all calculations, converged with respect to k -space integration. For CO on Ni we have also considered the bridge site. This site lacks the threefold-symmetry axis, and the irreducible wedge of the BZ zone is accordingly larger. The k points for these calculations were found by mapping out the points of the C_{3v} irreducible wedge to the actual symmetry-unique area, such that the sampling over the whole BZ was the same in all calculations.

The only degree of freedom in the geometry that we have considered is the metal adsorbate distance. For this purpose we have calculated with moderate precision the energy at an equidistant set of adsorbate-metal distances, obtaining the optimized distances given in Table III, which have an estimated accuracy of 0.2 bohr.

In this work we have employed the parametrization of Vosko, Wilk, and Nusair of the LDA correlation energy.³¹ We have therefore neglected the relativistic effect in the XC term. According to Engel, Keller, and Dreizler³² a relativistic correction to the GGA leads to improved atomic energies, but these improvements are much smaller than the relativistic effects introduced through the ZORA "kinetic" energy as discussed here. We have tested two forms of the GGA. The first, GGA(BP), employs Becke's correction for the exchange energy³³ and Perdew's correction for the correlation energy.³⁴ The second, GGA(PW), is due to Perdew and Wang.^{35,36} The GGA energy was evaluated at the LDA density rather than the GGA density, which has been shown to be an excellent approximation.³⁷

The Coulomb potential of the density has been obtained by expanding the density in a set of auxiliary basis functions³⁸ and calculating the potential from the fitted density. We have made sure that the deviation of the fitted density from the true density,

$$\left(\int (\rho - \rho_{\text{fit}})^2 dV \right)^{1/2}, \quad (10)$$

never exceeded 0.01 electrons. This quality of the density fit reduces errors due to this approximation to below the 0.01 eV level.

IV. RESULTS

In Table IV the results for the adsorption of CO on the (111) faces of Ni, Pd, and Pt are shown. We will first comment on the spin-polarization effects, and then discuss the influence of relativity on adsorption energy and site preference.

The differences between U and R results are in most cases quite small (between zero and a few hundredths of an eV), with lower adsorption energy in the spin-unrestricted case, and they are remarkably similar in the NR, SR, and FR cases. The effect is largest (in fact, only significant) for Ni,

TABLE IV. Adsorption energies (eV) of CO on the (111) faces of Ni, Pd, and Pt at one-third coverage. The calculations have been performed with a FR (including spin-orbit coupling), SR, or NR “kinetic-energy” operator and these three models have been combined with the U or R exchange-correlation functional with generalized gradient approximations according to Becke (exchange) and Perdew (correlation), GGA(BP). The geometries that were used are described in Table III. The basis functions were as shown in Table II, except that the f functions were omitted.

Metal	Site	Expt.	FR/ U	FR/ R	SR/ U	SR/ R	NR/ U	NR/ R
Ni	top		1.37	1.47	1.40	1.48	1.38	1.45
	bridge	1.3 ^a	1.50	1.67	1.48	1.63	1.47	1.63
	hollow		1.55	1.72	1.56	1.73	1.55	1.72
Pd	top		1.19	1.22	1.20	1.22	1.02	1.03
	hollow	1.5 ^b	1.47	1.49	1.48	1.51	1.42	1.45
Pt	top	1.3–1.5 ^c	1.29	1.29	1.41	1.42	0.83	0.83
	hollow		1.05	1.05	1.17	1.19	1.02	1.02

^aReferences 45 and 46.

^bReferences 47 and 48.

^cReferences 49–52.

notably for the bridge and hollow sites. For these sites the chemisorption energy of CO is reduced by about 0.16 eV when doing spin-unrestricted calculations instead of restricted ones. This can be traced to a larger spin polarization in the bare Ni slab, 4.1 electrons per unit cell, than in the CO covered situation, where it is, for instance, reduced to 2.8 electrons upon adsorption at the hollow site. Raatz and Salahub^{39,40} have explained the reduction of spin polarization after adsorption of CO on a Ni cluster by a transfer of electrons from occupied Ni d levels that are destabilized by the interaction with CO, to previously empty Ni d levels of opposite spin. For CO on Pd and Pt only very insignificant spin-polarization effects on the energy are seen. This does not imply that the calculations never yield any spin polarization, but in cases where they do spin-polarized solutions are practically degenerate with spin-restricted ones, so the energetic effects are negligible in any case.

Relativity has, in contrast, an important effect, notably for Pt, but also already for Pd (cf. Ref. 41). For top site adsorption energies, in particular, the effect is significant: for Pd the increase is 0.2 eV at either the SR or FR level, and for Pt it is 0.59 eV for SR (70% of the NR adsorption energy of 0.83 eV), which is, however, reduced to 0.46 eV for FR (i.e., by spin-orbit coupling effects). Although the magnitude of the relativistic effects is by far largest for Pt, the small effects in the other metals do exhibit the same trends (with an occasional exception): increase of the adsorption energy from NR to SR, and then decrease from SR to FR. These effects are by no means uniform for all adsorption sites. There is an important differential effect, the relativistic effects being clearly larger for top sites. For Pt not only the absolute magnitude of the effect is largest, but also the difference between the relativistic effects for top and hollow site is large. As a result, relativity changes the site preference from hollow at the NR level (0.19 eV more stable than top) to top at the FR level (0.24 eV more stable than hollow). Comparing to the experimental numbers, also given in Table IV, we note that experimentally for Pt the top site is indeed the preferred one. The

TABLE V. Comparison of the LDA and two GGA’s for the adsorption energies (eV) of CO.

Metal	Site	Model	LDA	GGA(BP)	GGA(PW)
Ni	hollow	SR/ U	2.73	1.56	1.72
Pd	hollow	SR/ R	2.59	1.48	1.61
Pt	top	SR/ R	2.33	1.41	1.55

experimental adsorption site is the hollow one on Pd, as correctly reproduced by the calculations. For Ni the calculated very small difference between the bridge and hollow site adsorption of CO, below the precision of our calculations, is not at variance with experiment, since at low coverage the threefold site is preferred and at one-third coverage the bridge sites are chosen, which suggests that these two sites are of similar stability and are more stable than the top site. In general the calculated energy differences between top and hollow site adsorption, being of the order of ~ 0.2 eV, are in support of the general notion, derived from experimental data, that the differences between CO bonded in top sites or in twofold or threefold sites of group-VIII metals is quite small.⁴² The absolute magnitude of the calculated adsorption energies is, with the GGA(BP) exchange-correlation functional, in satisfactory agreement with experiment for all three metals.

We have investigated the sensitivity of these results to choice of functional, by repeating the scalar relativistic calculations, at the theoretically most stable sites, with two other functionals, LDA and GGA(PW), see Table V. In line with previous studies^{43,44} it is seen that the GGA improves dramatically on the LDA. GGA(BP) reduces chemisorption energies with respect to the severely overbinding LDA somewhat more strongly than GGA(PW) does, but the quality of these two GGA’s is similar.

In order to shed some light on the working of relativity we have gathered some Mulliken populations in Table VI pertaining to the case of CO on Pt, comparing relativistic and nonrelativistic populations of the bare slab and the top and hollow site adsorbed systems. Presented are the 5σ and 2π populations from the CO overlayer, and the populations of the top layer Pt atom closest to the adsorbate. For the hollow site geometry one of the three equivalent top layer Pt atoms is meant. Many aspects of the relativistic effect can be understood by considering the Pt atom. In the free Pt atom relativity stabilizes and contracts the $6s$ orbital considerably, the $6p$ orbital is also contracted but not stabilized, and the radius and eigenvalue of the $5d$ orbital are slightly reduced. In all the slab calculations the effect of the stabilization of the $6s$ orbital can be seen in the increase of the Pt s populations. The p populations are increased as well with the exception of the top site $p(\sigma)$ population. The stabilization of the $6s$ orbital makes it a much better acceptor, and the contraction brings its radius closer to the radius of the $5d$ orbital. On this basis an enhanced donation-backdonation with the CO 5σ and 2π orbitals through relativity is to be expected, which is in agreement with the observed 5σ and 2π populations. However, the relativistic effect is not caused by an increased donation from the d orbitals: the d population is reduced on adsorption, but the change is the same in the SR and NR case. The p orbitals do play an important role

TABLE VI. Mulliken populations for CO and Pt in relativistic and nonrelativistic calculations for the bare slab and the systems with CO adsorbed at the top or at the hollow site. The populations specified are the 5σ and 2π orbitals from the CO overlayer and the Pt s , p , and d populations are indicated from the atom closest to the adsorbate (at hollow site one of the three equivalent atoms is taken). The p and d populations have been split up in contributions according to the number of lobes of the basis functions in the x - y plane, being 0, 1, or 2 labeled as σ , π , and δ , respectively.

System	Model	5σ	2π	s	$p(\sigma)$	$p(\pi)$	$p(\text{tot})$	$d(\sigma)$	$d(\pi)$	$d(\delta)$	$d(\text{tot})$
Bare slab	NR			0.56	0.09	0.26	0.35	1.78	3.83	3.46	9.07
Bare slab	SR			0.86	0.14	0.32	0.46	1.68	3.71	3.29	8.68
CO at top	NR	1.60	0.37	0.63	0.20	0.38	0.58	1.54	3.76	3.64	8.94
CO at top	SR	1.58	0.44	0.82	0.18	0.48	0.66	1.38	3.68	3.49	8.55
CO at hollow	NR	1.53	0.56	0.51	0.13	0.25	0.38	1.81	3.70	3.54	9.05
CO at hollow	SR	1.45	0.67	0.80	0.16	0.33	0.49	1.74	3.55	3.35	8.64

in the interaction but the population changes are fairly insensitive to relativity. The difference between the two models appears to be related to the change in s population. At the top site the change is nonrelativistically 0.07 electrons whereas it is -0.04 in the SR calculations. At the hollow site the change is according to both models about -0.05 electrons. From all this the picture emerges that the contraction of the $6s$ orbital is the most important effect and that it is relatively more important at the onefold site with the shorter C-Pt distance than at the threefold hollow site.

In conclusion, the ZORA-APA is an efficient and accurate method to do relativistic calculations that can successfully be combined with the frozen-core approximation. Our calculations have shown a reduction of the interaction between CO and the Ni surface by spin polarization. On Pt relativity is

essential to predict correctly not only the adsorption energy, but also the adsorption site. On this surface the molecule adsorbate interaction is reduced by the spin-orbit coupling. Once more the inclusion of gradient corrections in the XC functional proves to be essential as the LDA greatly overestimates the interactions.

ACKNOWLEDGMENTS

This work was supported by the Netherlands Foundation for Chemical Research (SON), with financial aid from the Netherlands Organization for Scientific Research (NWO). Extensive use was made of the supercomputing facilities of the National Computing Facilities Foundation (NCF).

- ¹J. G. Snijders and E. J. Baerends, Mol. Phys. **36**, 1789 (1978).
- ²J. G. Snijders, E. J. Baerends, and P. Ros, Mol. Phys. **38**, 1909 (1979).
- ³T. Ziegler, J. G. Snijders, and E. J. Baerends, J. Chem. Phys. **74**, 1271 (1981).
- ⁴P. M. Boerrigter, Ph.D. thesis, Vrije Universiteit, Amsterdam, The Netherlands, 1987.
- ⁵T. Ziegler *et al.*, J. Phys. Chem. **93**, 3050 (1989).
- ⁶V. A. Nasluzov and N. Rösch, Chem. Phys. **210**, 413 (1996).
- ⁷G. B. Bachelet, D. R. Hamann, and M. Schlüter, Phys. Rev. B **26**, 4199 (1982).
- ⁸E. van Lenthe, E. J. Baerends, and J. G. Snijders, J. Chem. Phys. **99**, 4597 (1994).
- ⁹E. van Lenthe, E. J. Baerends, and J. G. Snijders, J. Chem. Phys. **101**, 9783 (1994).
- ¹⁰R. van Leeuwen, E. van Lenthe, E. J. Baerends, and J. G. Snijders, J. Chem. Phys. **101**, 1272 (1994).
- ¹¹P. M. Boerrigter, G. te Velde, and E. J. Baerends, Int. J. Quantum Chem. **33**, 87 (1988).
- ¹²E. van Wezenbeek, E. J. Baerends, and J. G. Snijders, Theor. Chim. Acta **81**, 139 (1991).
- ¹³S. C. Chung, S. Krüger, G. Pacchioni, and N. Rösch, J. Chem. Phys. **102**, 3695 (1995).
- ¹⁴J. Li, G. Schreckenbach, and T. Ziegler, J. Am. Chem. Soc. **117**, 486 (1995).
- ¹⁵P. P. Singh, Phys. Rev. Lett. **72**, 2446 (1994).
- ¹⁶P. P. Singh, Phys. Rev. B **49**, 4954 (1994).
- ¹⁷L. Szunyogh, B. Újfalussy, P. Weinberger, and J. Kollár, J. Phys. Condens. Matter **6**, 3301 (1994).
- ¹⁸V. Drchal, J. Kudrnovsky, and P. Weinberger, Phys. Rev. B **50**, 7903 (1994).
- ¹⁹G. te Velde and E. J. Baerends, Phys. Rev. B **44**, 7888 (1991).
- ²⁰G. Wiesenekker, G. J. Kroes, and E. J. Baerends, J. Chem. Phys. **104**, 7344 (1996).
- ²¹G. J. Kroes, G. Wiesenekker, E. J. Baerends, and D. Neuhauser, J. Chem. Phys. **105**, 5979 (1996).
- ²²G. Blyholder, J. Phys. Chem. **68**, 2772 (1964).
- ²³B. Hammer, Y. Morikawa, and J. K. Nørskov, Phys. Rev. Lett. **76**, 2141 (1996).
- ²⁴Y.-T. Wong and R. Hoffmann, J. Phys. Chem. **95**, 859 (1995).
- ²⁵E. van Lenthe, J. G. Snijders, and E. J. Baerends, J. Chem. Phys. **105**, 6505 (1996).
- ²⁶G. te Velde and E. J. Baerends, J. Comput. Phys. **99**, 84 (1992).
- ²⁷O. Gunnarsson and B. I. Lundqvist, Phys. Rev. B **13**, 4274 (1976).
- ²⁸P. H. T. Philipsen, G. te Velde, and E. J. Baerends, Chem. Phys. Lett. **226**, 583 (1994).
- ²⁹G. Wiesenekker, G. J. Kroes, E. J. Baerends, and R. C. Mowrey, J. Chem. Phys. **102**, 3873 (1995).
- ³⁰A. Rosa *et al.*, J. Phys. Chem. **100**, 5690 (1994).

- ³¹S. H. Vosko, L. Wilk, and M. Nusair, *Can. J. Phys.* **58**, 1200 (1980).
- ³²E. Engel, S. Keller, and R. M. Dreizler, *Phys. Rev. A* **53**, 1367 (1996).
- ³³A. D. Becke, *Phys. Rev. A* **38**, 3098 (1988).
- ³⁴J. P. Perdew, *Phys. Rev. B* **33**, 8822 (1986).
- ³⁵J. P. Perdew, *Electronic Structure of Solids '91* (Akademie Verlag, Berlin, 1991).
- ³⁶J. P. Perdew *et al.*, *Phys. Rev. B* **46**, 6671 (1992).
- ³⁷L. Fan and T. Ziegler, *J. Chem. Phys.* **94**, 6057 (1991).
- ³⁸E. J. Baerends, D. E. Ellis, and P. Ros, *Chem. Phys.* **2**, 42 (1973).
- ³⁹F. Raatz and D. R. Salahub, *Surf. Sci. Lett.* **146**, 609 (1984).
- ⁴⁰F. Raatz and D. R. Salahub, *Surf. Sci.* **176**, 219 (1986).
- ⁴¹R. A. Olsen *et al.*, *J. Chem. Phys.* **106**, 9286 (1997).
- ⁴²B. E. Nieuwenhuys, *Surf. Sci.* **126**, 307 (1983).
- ⁴³P. H. T. Philipsen and E. J. Baerends, *Phys. Rev. B* **54**, 5326 (1996).
- ⁴⁴P. Hu *et al.*, *Chem. Phys. Lett.* **230**, 501 (1994).
- ⁴⁵J. B. Miller *et al.*, *J. Chem. Phys.* **87**, 6725 (1987).
- ⁴⁶J. C. Campuzano and R. G. Greenler, *Surf. Sci.* **83**, 301 (1979).
- ⁴⁷H. Conrad, G. Ertl, J. Koch, and E. E. Latta, *Surf. Sci.* **43**, 462 (1974).
- ⁴⁸H. Ohtani, M. A. van Hove, and G. A. Somorjai, *Surf. Sci.* **187**, 372 (1987).
- ⁴⁹R. W. McCabe and L. D. Schmidt, *Surf. Sci.* **65**, 189 (1977).
- ⁵⁰G. Ertl, M. Neumann, and K. M. Streit, *Surf. Sci.* **64**, 393 (1977).
- ⁵¹H. Steiniger, S. Lehwald, and H. Ibach, *Surf. Sci.* **123**, 264 (1982).
- ⁵²B. E. Hayden and A. M. Bradshaw, *Surf. Sci.* **125**, 787 (1983).