and 13.7, respectively. The observed ratios are 28.8 and 13.8, giving differences of 1.4% and 0.7%, respectively, which is quite satisfactory. Because we were unable to assign individual frequencies to a particular isomer in the spectra of $CH_3(CD_3)NPF_2$, we compared the product of the ratios for both isomers. The observed quantities, 27.6 for A′ and 13.0 for A″, deviate by 2.8 and 4.4%, respectively, from the theoretical values. Therefore, the Teller–Redlich product rule supports the proposed vibrational assignment.

The fit of the frequencies arising from the PF_2 torsion was very good. The value of 4356 cm^{-1} obtained for the barrier to internal rotation is much larger than the values of 1000–2000 cm^{-1} for

a "typical" torsion around a single bond. This high barrier value along with the short PN bond distance indicates that there is considerable π bonding between the nitrogen and phosphorus atoms with the nitrogen having an sp^2 hybridization. The results of this study would make the investigation of pentavalent aminophosphines interesting in order to determine if a planar structure and a short PN bond length is maintained for these compounds.

Calculation of Bond Energies in Compounds of Heavy Elements by a Quasi-Relativistic Approach

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A quasi-relativistic method, in which the valence density is optimized with respect to the first-order relativistic Hamiltonian, has been evaluated by calculations on systems containing heavy elements including third-row transition metals and actinides. The method adopts the statistical energy expression and employs in addition the frozen core approximation. The quasi-relativistic method has been applied in calculations on atomic orbital energies for the valence shells of heavy elements. It is concluded from these calculations that the quasi-relativistic scheme affords results in better accord with the fully relativistic Dirac–Slater method than the first-order relativistic method based on perturbation theory. Calculations on the M–X bond energies in MX_4 (M = Th, U; X = F, Cl, Br, I) as well as the M–R bond energies in Cl_3MR (M = Th, U; R = H, CH_3) revealed in addition that bond energies based on the quasi-relativistic method (QR) were in better agreement with experimental data than bond energies based on the first-order perturbation theory (FO). The absolute mean deviations with respect to experimental values were 6.9 and 16.5 kcal mol^{-1} for QR and FO, respectively, in the case of the MX_4 systems. It is concluded that the quasi-relativistic method, in which changes in the electron density induced by relativity ($\Delta\rho^R$) are approximately taken into account in the energy expression, should be used for compounds containing actinides. Both QR and FO (in which contributions from $\Delta\rho^R$ to the total energy are absent, even though they are present in the orbital energies) are appropriate for elements up to $Z = 80$, although QR represents a slight improvement for the elements in the third transition series. The calculated bond energies included contributions from a nonlocal correction to the statistical exchange potential as well as a potential representing correlation between electrons of different spins.

I. Introduction

It has become possible over the last decade to carry out calculations on compounds of heavy elements, taking relativistic effects into account explicitly. The methodology ranges from fully relativistic calculations[1] based on the many-electron Dirac–Hamiltonian to methods employing effective relativistic core potentials,[2] first-order perturbation theory,[3] quasi-relativistic approaches,[4] and scalar Hamiltonians.[5] Advances in the com-

putational techniques dealing with relativistic effects have been reviewed[6] within the last years, and comprehensive discussions[7] on the chemical importance of relativistic effects have also appeared.

We have recently studied[8] the influence of relativistic effects on the periodic trends within a triad of transition metals, employing the relativistic first-order perturbation method by Snijders et al.[3,9,10]

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It was shown in this[8] and related studies[11,12] that relativistic effects (in most cases) will increase the strength of chemical bonds containing 5d elements (W, Au, etc.) and further shorten the same bonds by up to 0.2 Å. We were in addition able to furnish a clear physical picture[8,11d,12] of the two effects, according to which both bond-shortening and (in most cases) bond-strengthening are caused by a first-order relativistic reduction in the kinetic energy of the electrons. It was finally concluded from this[8] and other studies[11] that the relativistic first-order perturbation method[3] is adequate for elements up to mercury with $Z = 80$, although the first-order method does not include any contribution to the total energy from changes in the electron density induced by relativity.

Beyond the third transition series one finds, at higher atomic numbers, the actinides. The chemistry of actinides, in particular in the organometallic subfield,[13] is an active area of research, and this field has also attracted the attention of theoreticians.[10,14] We shall here demonstrate that the first-order perturbation theory[3] is inadequate for bond energy calculations on systems containing elements as heavy as the actinides. That is, we shall show that the change in the valence density ($\Delta\rho^R_{val}$) induced by relativity is too large to be neglected in energy calculations on these systems. We shall further show that one can incorporate the influence of $\Delta\rho^R_{val}$ on the total energy approximately and efficiently by resorting to a quasi-relativistic approach.

Quasi-relativistic methods have been discussed in the past.[4] However, they have not to our knowledge been applied to bond energy calculations. The quasi-relativistic method will be applied, in conjunction with Becke's[15] newly developed density functional and the HFS-LCAO program system due to Baerends[16] et al., to the M–X bond energies in MX_4 (M = Th, U; X = F, Cl, Br, I) as well as the M–R bond energies in Cl_3MR (M = Th, U; R = H, CH$_3$). Becke's functional[15] has recently been shown to provide quantitative estimates of bond energies in main-group compounds[15,17] as well as metal–ligand[12f-i] and metal–metal[12e] bonds of transition-metal complexes. A quasi-relativistic extension, appropriate for actinides, should thus make Becke's and related[18] approximate density functionals applicable to calculations on bond energies in compounds containing any element in the periodic chart.

II. Method

A. The Nonrelativistic HFS Method. The many-electron wave function Ψ^0 is in the HFS method represented by a single Slater determinant

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$$\Psi^0 = |\phi^0(1)\ \phi_2^0(2)\ ...\ \phi_i^0(i)\ \phi_j^0(j)\ ...\ \phi_n^0(n)| \quad (1)$$

where $\{\phi_i^0(i), i = 1, n\}$ is a set of spin orbitals.

The total energy expression in the HFS theory, ofter referred to as the statistical energy expression E_{HFS}, can be derived from the expectation value $\langle\Psi^0|H^0|\Psi^0\rangle$ with respect to the nonrelativistic Hamiltonian

$$H^0 = -\frac{1}{2}\sum_{i=1}^{i=n}\nabla_i^2 + \sum_{i=1}^{i=n}V_N(\mathbf{r}_i) + \frac{1}{2}\sum_{i\neq j}1/|\mathbf{r}_i - \mathbf{r}_j| \quad (2)$$

by invoking the statistical exchange approximation.[19] The statistical energy expression E_{HFS} reads in terms of the one-electron density matrix $\rho^0(1,1')$ and the electron density $\rho^0(\mathbf{r}_1)$:

$$E_{HFS} = -\frac{1}{2}\int_{1\rightarrow 1'}\nabla_i^2\rho^0(1,1')\ d\mathbf{X}_1 +$$
$$\int\rho^0(\mathbf{r}_1)\left[V_N(\mathbf{r}_i) + \frac{1}{2}V_c(\rho^0,\mathbf{r}_1) + \frac{3}{4}V_x(\rho^0(\mathbf{r}_1))\right]d\mathbf{r}_1 \quad (3)$$

Here $V_x(\rho^0(\mathbf{r}_1))$, characteristic for the statistical exchange expression, is given by

$$V_x(\rho^0(\mathbf{r}_1)) = -3\alpha_{ex}\left[\frac{3}{8\pi}\rho^0(\mathbf{r}_1)\right]^{1/3} \quad (4)$$

where α_{ex}, the so-called exchange scale factor, is taken to be 0.7. Further,

$$V_c(\rho^0,\mathbf{r}_1) = \int\rho^0(\mathbf{r}_2)/|\mathbf{r}_1 - \mathbf{r}_2|\ d\mathbf{r}_2 \quad (5)$$

The set of spin orbitals $\{\phi_i^0(i), i = 1, n\}$ for which E_{HFS} is optimal can be found from the following set of one-electron HFS equations

$$f^0(1)\ \phi_i^0(1) = \epsilon_i\phi_i^0(1) \quad (6)$$

where the nonrelativistic one-electron HFS operator is defined as

$$f^0(1) = -\frac{1}{2}\nabla_1^2 + V_N(\mathbf{r}_1) + V_c(\rho^0,\mathbf{r}_1) + V_x(\rho^0(\mathbf{r}_1)) \quad (7)$$

It is expedient in molecular calculations to adopt the frozen core approximation[16a] in which orbitals $\{\chi_i\}$ of lower energy are taken from the constituting atoms under the assumption that the set $\{\chi_i\}$ is unperturbed on molecular formation. The valence orbitals $\{\phi_i^0(i)\}$ are then determined from eq 6 under the constraint that the valence orbitals must be orthogonal to the core set $\{\chi_i\}$. We shall often divide the total density into core and valence parts as $\rho^0 = \rho^0_{core} + \rho^0_{val}$ in connection with the frozen core approximation.

B. Relativistic HFS Method Based on First-Order Perturbation Theory. It is possible to extend Dirac's[20] relativistic theory for the hydrogen atom to many-electron systems by neglecting retardation as well as certain magnetic effects. Dirac's Hamiltonian for a many electron system can be written as

$$H^D = \sum_{i=1}^{i=n}h_D(i) + \sum_{i=1}^{i=n}V_N(\mathbf{r}_i) + \frac{1}{2}\sum_{i\neq j}1/|\mathbf{r}_i - \mathbf{r}_j| \quad (8)$$

where

$$h_D(i) = c\vec{\alpha}(i)\cdot\vec{p}(i) + c^2\beta(i) \quad (9)$$

In eq 9 $\alpha_j(i), j = 1, 2, 3$, and $\beta(i)$ are the 4 × 4 Dirac matrices, $\vec{p}(i)$ is the momentum operator, and c is the velocity of light.

The simplest possible wave function Ψ^D in the many-electron Dirac theory is a Slater determinant of the form given in eq 1 where the set of spin orbitals $\{\phi_i^0(i)\}$ are replaced by a set of four-component Dirac spinors $\{a^i(i)\}$. Ellis[21] has shown (at least for valence electrons) that it is justified to apply the statistical

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exchange approximation to $\langle \Psi^D | H^D | \Psi^D \rangle$, and thus obtain the relativistic (Dirac–Slater) statistical energy expression

$$E_{DS} = \int_{1 \to 1'} h_D(1) \, \rho^{DS}(1,1') \, dX_1 +$$
$$\int \rho^{DS}(\mathbf{r}_1)[V_N(\mathbf{r}_i) + \tfrac{1}{2} V_c(\rho^{DS}, \mathbf{r}_1) + \tfrac{3}{4} V_x(\rho^{DS}(\mathbf{r}_1))] \, d\mathbf{r}_1 \quad (10)$$

The optimal set of Dirac spinors $\{a^l(i)\}$ can further be determined from the Dirac–Slater one-electron equations

$$\{h_D(1) + V_N(\mathbf{r}_1) + V_c(\rho^{DS}, \mathbf{r}_1) + V_x(\rho^{DS}(\mathbf{r}_1))\} a^l(1) = \epsilon_i a^i(1) \quad (11)$$

Equation 11 is considerably more complicated to solve than eq 7 due to the four, in general complex, components of the Dirac orbitals a^l. It has further proven difficult[1,6c] to apply the linear combination of atomic orbital (LCAO) approach in solving eq 11 or the corresponding Dirac–Fock equation for molecular systems. That is, basis sets larger than normal are required in order to avoid a collapse into negative energy states in variational calculations based on H^D or E_{DS}.

There are several ways in which eq 11 can be simplified, and we shall here follow the perturbational approach due to Snijders and Baerends.[3] The perturbational approach starts from the Hamiltonian

$$H^{FW} = \sum_{i=1}^{i=n} \left\{ -\frac{1}{2} \nabla_i^2 + V_N(i) - \frac{\alpha^2}{8} \nabla_i^4 + \frac{\alpha^2}{8} \nabla_i^2 V_N(i) + \right.$$
$$\frac{\alpha^2}{4} \sigma(i) \cdot [\nabla V_N(i) \times \mathbf{p}(i)] \bigg\} + \sum_{i<j} \left\{ \frac{1}{r_{ij}} + \frac{\alpha^2}{8} [\nabla_i^2 + \nabla_j^2] \frac{1}{r_{ij}} + \right.$$
$$\left. \frac{\alpha^2}{4} \sigma(i) \cdot \left[\nabla(i) \left(\frac{1}{r_{ij}} \right) \times \mathbf{p}(i) \right] + \frac{\alpha^2}{4} \sigma(j) \cdot \left[\nabla(j) \left(\frac{1}{r_{ij}} \right) \times \mathbf{p}(j) \right] \right\} \quad (12)$$

obtained from eq 8 by a sequence of Foldy–Wouthuysen transformations[22] in which terms up to order α^2 are retained, where α is the fine structure constant. The Hamiltonian H^{FW} does not contain any operator connecting the large and small components in the Dirac spinors a^i, and the many-electron wave function in eq 1 can as a consequence be constructed from a set of spin orbitals $\{\phi_i^{FW}(i)\}$ as in the nonrelativistic case. In the perturbational approach the optimal spin orbitals $\phi_i^{FW}(i)$ and corresponding orbital energies ϵ_i^{FW} are determined up to α^2 as $\phi_i^{FW}(i) = \phi_i^0(i) + \phi_i^1(i)$ and $\epsilon_i^{FW} = \epsilon_i^0 + \epsilon_i^1$, respectively, where $\phi_i^0(i)$ is the nonrelativistic spin orbital with the orbital energy ϵ_i^0. The first-order corrections $\phi_i^1(i)$ and ϵ_i^1 are further found from first-order perturbation theory as solutions to the set of equations

$$(f^0 - \epsilon_i^0) \phi_i^1(1) = -(f^1 - \epsilon_i^1) \phi_i^0(1) \quad (13)$$

In eq 13 f^0 is the nonrelativistic HFS operator given in eq 7. The operator f^1 can essentially (see ref 8) be written as

$$f^1(1) = -\frac{\alpha^2}{8} \nabla_1^4 + \frac{\alpha^2}{8} \nabla_i^2 V_N(1) +$$
$$\frac{\alpha^2}{8} \sigma(1) \cdot [\nabla(V_N(1) + V_c(\rho^0_{core}, \mathbf{r}_1)) \times \mathbf{p}(1)] + V_{el}(1)$$
$$= h_{mv} + h_{dw} + h_{so} + V_{el}$$
$$= h^1 + V_{el} \quad (14)$$

where

$$V_{el}(1) = \int \rho^1(\mathbf{r}_2)/\mathbf{r}_{12} \, d\mathbf{r}_2 - \alpha_{ex}\left(\frac{3}{8\pi}\right)^{1/3} [\rho^0(\mathbf{r}_1)]^{-2/3} \rho^1(\mathbf{r}_1) \quad (15)$$

In eq 15 ρ^0 represents the nonrelativistic density and

$$\rho^1(\mathbf{r}_1) = \sum_{i=1}^{i=n} \{\phi_i^1(1) \, \phi_i^0(1)^* + \phi_i^1(1)^* \, \phi_i^0(1)\} \quad (16)$$

the first-order change in the electronic density due to relativistic effects. Note that eq 13 has to be solved iteratively since f^1 depends on $\phi_i^1(1)$ through V_{el}. The first-order change in the total statistical energy due to relativity is given by[8]

$$E^1 = \int_{1 \to 1'} h^1(1) \, \rho^0(1,1') \, dX_1 \quad (17)$$

The first-order change E^1 does not depend on ρ^1 if the nonrelativistic set of spin orbitals $\{\phi_i^0(i)\}$ is determined variationally.

Electronic systems for which relativistic effects are of importance contain one or more heavy elements with large cores. As a consequence much can be gained in terms of computational efficiency by adopting the frozen core approximation according to which only the valence orbitals are considered in eq 16. It is further appropriate in systems containing heavy elements only to apply the first-order relativistic treatment to the valence electrons. That is, relativistic effects are much too large in the core region of heavy elements for a first-order theory to be applicable. The frozen core approximation is introduced[3] by writing

$$\rho^1(\mathbf{r}_1) = \rho^1_{val}(\mathbf{r}_1) + \Delta\rho^R_{cor}(\mathbf{r}_1) \quad (18)$$

where ρ^1_{val} is the first-order change in the valence density due to relativistic effects. Further, $\Delta\rho^R_{cor}$ is obtained from atomic calculations as $\Delta\rho^R_{cor} = \rho^R_{cor} - \rho^0_{cor}$, where ρ^0_{cor} is the core density from a nonrelativistic HFS calculation and ρ^R_{cor} the core density from a Full Dirac–Slater calculation.

In a first-order relativistic treatment of the valence electrons it is consistent to orthogonalize the valence set $\{\phi_i^0(i) + \phi_i^1(i), i = 1, n_v\}$ to the zero order (i.e., nonrelativistic) core orbitals. This is the procedure actually followed. However, note that the potential from the relativistic core orbitals $\{a^l\}$ is taken into account to all orders through eq 18.

C. The Quasi-Relativistic Approach. The appearance of the mass-velocity term $-\nabla_i^4$ in the Hamiltonian H^{FW} of eq 12 precludes a direct optimization of the expectation value $\langle \Psi | H^{FW} | \Psi \rangle$ with respect to a determinantal wave function of the form given in eq 1. The first-order operator H^{FW} is not Hermitian and it has, if only the usual boundary conditions are applied, a continuous eigenvalue spectrum without lower bound. We will, however, restrict this operator to the space of the solutions of the zero-order (nonrelativistic) Hamiltonian. Within this restricted space H^{FW} of eq 12 is Hermitian. Equivalently, the requirement that $H^0 \Psi$ obeys the boundary conditions, which is automatically fulfilled if Ψ can be expanded in a uniformly convergent series of eigenfunctions of H^0, may be looked upon as an additional set of boundary conditions which lead to quantization of the fourth-order differential equation. The so-called quasi-relativistic approach of diagonalizing the first-order H^{FW} in the space of zero-order solutions is therefore formally justified. Compared to straightforward first-order perturbation theory, higher order corrections due to h^1 are in this way taken into account and relativistic density changes are incorporated in the total energy. On the other hand, perturbation terms in the Hamiltonian beyond first order are still completely neglected. It is not clear a priori that the quasi-relativistic approach will constitute a significant improvement over first-order calculations. In this paper, we investigate, by comparing to full Dirac–Slater calculations and to experiment, to what extent this is the case.

According to the numerical results to be presented in this work, and the experience of others,[4] the quasi-relativistic approach seems well justified. However, even if very little numerical change is to be expected, a more satisfactory procedure would clearly be based on two-component Pauli-like effective Hamiltonians.[22,23] Work is in progress to construct such a variationally stable Hamiltonian without, however, sacrificing the computational efficiency of the present approach.

The expression for $\langle \Psi | H^{FW} | \Psi \rangle$ reads after invoking the statistical exchange approximation

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$$E^{QR} = \int_{1\rightarrow1'} [-\tfrac{1}{2}\nabla_1^2 + V_N(1) + h^1(1)]\rho_v{}^{QR}(1,1')\ dX_1 +$$
$$\int \rho_t(1)[\tfrac{1}{2}V_c(\rho_t,r_1) + \tfrac{3}{4}V_x(\rho_t(r_1))]\ dr_1 \quad (19)$$

We have in eq 19 omitted constant core terms. Further, some numerically insignificant relativistic terms (see ref 8) involving two-electron integrals over valence orbitals have been neglected. The total density $\rho_t(r_1)$ is given as $\rho_t(r_1) = \rho_v{}^{QR}(r_1) + \rho^R{}_{cor}(r_1)$, where the core density $\rho^R{}_{cor}(r_1)$ is taken from atomic Dirac–Slater calculations.

An optimization of eq 20 with respect to the valence density $\rho_v{}^{QR}$ affords the following set of quasi-relativistic one-electron equations

$$[-\tfrac{1}{2}\nabla_1^2 + V_N(1) + h^1(1) + V_c(\rho_t,r_1) + V_x(\rho_t(r_1))]\phi_i{}^{QR}(1) =$$
$$\epsilon_i{}^{QR}\phi_i{}^{QR}(1) \quad (20)$$

for the valence set $\{\phi_i{}^{QR}, i = 1, n_v\}$. As already noted, the orbitals $\phi_i{}^{QR}$ contain corrections to $\phi_i{}^0$ in all orders of α^2 with respect to h^1, but corrections to $\phi_i{}^0$ from operators of order α^4 or higher are neglected.

III. Computational Details

All calculations were based on the newest vectorized[23] version of the HFS program system[16] or its relativistic extension.[3] The Slater-type basis[24] employed was of double-ζ quality for the main-group elements and of triple-ζ quality for the transition metals and actinides. The ns and np orbitals on the main-group elements and the ns, np, nd, $(n + 1)s$, and $(n + 1)p$ on the transition metals were considered as valence orbitals. The valence set on the actinides included 6s, 6p, 6d, 5f, 7s, and 7p. The remaining orbitals of lower energy were frozen according to the method due to Baerends[16] et al. A set of auxiliary s, p, d, f, and g STO functions[25] centered on all nuclei were used in order to fit the molecular density and represent the Coulomb and exchange potentials accurately in each SCF cycle.

The molecular calculations presented in section V were in the nonrelativistic case based on the energy expression

$$E^0{}_{SB} = E_{HFS} + E_c[\rho^0] + E_x{}^{NL}[\rho^0] \quad (21a)$$

where the term E_c, proposed by Stoll[26] et al., takes into account correlation between electrons of different spins, whereas $E_x{}^{NL}$, due to Becke,[15] is a nonlocal correction to the purely local exchange potential V_x. The two correction terms E_c and $E_x{}^{NL}$ have been shown[11e–i,15,17] to improve the accuracy of calculated bond energies considerably. In the relativistic first-order calculations on molecular systems the term E^1 defined in eq 17 was added to $E^0{}_{SB}$. We applied for the molecular quasi-relativistic calculations the following energy expression

$$E^{QR}_{SB} = E^{QR} + E_c[\rho_t] + E_x{}^{NL}[\rho_t] \quad (21b)$$

where the correction terms E_c and $E_x{}^{NL}$ now are with respect to the total density ρ_t defined in section II.

The molecular geometries were, unless otherwise stated, fully optimized. Note that α_{ex} (see eq 4) in the energy expressions of eq 21a and 21b has the value of $2/3$, in accordance with the nonlocal theory of Becke.[15]

IV. Atomic Calculations

We shall here compare atomic orbital energies calculated by the fully relativistic DS method (eq 11) with the corresponding energies calculated by the first-order theory[3] (eq 13), the quasi-relativistic method (eq 20), and the nonrelativistic HFS scheme (eq 7). We shall in our comparison primarily be concerned with the degree to which the approximate first-order theory (FO) and the quasi-relativistic method (QR) reproduce results from fully

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TABLE I: A Comparison of Nonrelativistic, First-Order Perturbation, Quasi-Relativistic and Relativistic Dirac–Slater Orbital Energies for Br, I, Hg, and U (in eV)[a]

	nonrelat	perturbn calcn (error)	quasi-relat calcn (error)	Dirac–Slater
Br				
4s$_{1/2}$	18.73	19.38 (5.8)	19.42 (0.0)	19.42
4p$_{1/2}$	7.18	7.44 (10.3)	7.49 (6.9)	7.47
4p$_{3/2}$		6.95 (4.5)	6.89 (9.8)	6.96
I				
5s$_{1/2}$	15.37	16.55 (13.0)	16.89 (13.0)	16.72
5p$_{1/2}$	6.45	6.97 (15.0)	7.00 (9.8)	7.06
5p$_{3/2}$		6.04 (0.0)	6.04 (0.0)	6.04
Hg				
5d$_{3/2}$	11.52	10.40 (1.8)	10.37 (0.8)	10.38
5d$_{5/2}$		8.61 (3.0)	8.67 (5.0)	8.52
6s$_{1/2}$	4.80	5.75 (37.0)	6.16 (9.3)	6.30
U				
6s$_{1/2}$	35.33	42.74 (35.5)	47.55 (6.5)	46.81
6p$_{1/2}$	21.62	26.19 (38.9)	27.58 (20.4)	29.11
6p$_{3/2}$		20.07 (6.2)	20.19 (1.6)	20.16
5f$_{5/2}$	9.31	2.60 (3.2)	2.46 (5.3)	2.81
5f$_{7/2}$		1.51 (6.7)	1.78 (3.1)	2.00
6d$_{3/2}$	3.15	1.83 (8.7)	1.90 (2.5)	1.93
6d$_{5/2}$		1.24 (13.2)	1.46 (0.0)	1.46
7s$_{1/2}$	2.92	3.27 (51.2)	3.61 (5.3)	3.65

[a] An estimate of the error (in percentage) in the relativistic corrections calculated by perturbation theory and the quasi-relativistic method is given in parentheses.
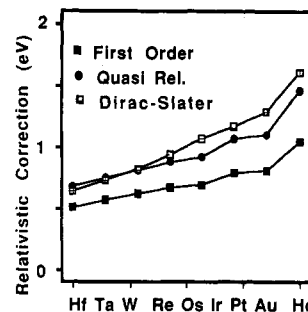

Figure 1. Relativistic corrections to the 6s orbital energies of elements in the third-row transition series from first-order, quasi-relativistic, and Dirac–Slater calculations.
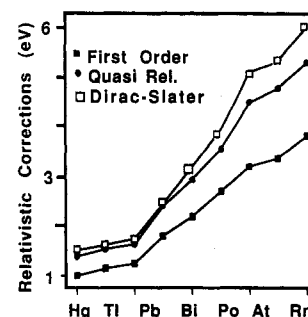

Figure 2. Relativistic corrections to the 6s orbital energies of elements in the posttransition series (Hg to Ra) from first-order, quasi-relativistic, and Dirac–Slater calculations.

relativistic DS calculations as we proceed through the periodic chart toward elements of higher atomic number.

Calculated orbital energies for a cross section of elements are displayed in Table I from ref 4c. The results given in Table I for bromine and iodine are typical for calculations on elements up to $Z = 54$, in that relativistic corrections to the energies of the valence orbitals are modest and well reproduced by FO as well as QR. We shall by relativistic corrections understand the difference between nonrelativistic orbital energies and orbital energies calculated by the FO, QR, and DS methods.

The first discrepancy between the FO and QR methods occurs in the third transition series (Hf–Hg) with $Z = 72$ to 80. The

TABLE II: A Comparison of 6p Orbital Energies (in eV) for Tl to Ra, Calculated by the Nonrelativistic, First-Order Perturbation, Quasi-Relativistic, and Dirac–Slater Methods

	nonrelat 6p	perturbn $6p_{1/2}$	perturbn $6p_{3/2}$	quasi-relat $6p_{1/2}$	quasi-relat $6p_{3/2}$	Dirac–Slater $6p_{1/2}$	Dirac–Slater $6p_{3/2}$
Tl	2.08	2.19	1.48	2.27	1.47	2.35	1.37
Pb	3.13	3.33	2.29	3.45	2.26	3.45	2.09
Bi	4.13	4.65	3.28	4.86	3.28	5.00	3.14
Po	5.12	6.02	4.26	6.33	4.27	6.53	4.14
At	6.13	7.30	5.25	7.70	5.27	8.10	5.12
Rn	7.13	8.69	6.28	9.16	6.26	9.72	6.11
Fr	11.90	13.71	10.60	14.40	10.60	14.97	10.35
Ra	16.50	18.66	14.70	19.53	14.70	20.14	14.43

TABLE III: A Comparison of 5f Orbital Energies (in eV) for the Actinides Th to Lr Calculated by the Nonrelativistic, First-Order Perturbation, Quasi-Relativistic, and Dirac–Slater Methods

	nonrelat 5f	perturbn $5f_{5/2}$	perturbn $5f_{7/2}$	quasi-relat $5f_{5/2}$	quasi-relat $5f_{7/2}$	Dirac–Slater $5f_{5/2}$	Dirac–Slater $5f_{7/2}$
Th	9.61	2.65	1.86	3.28	2.68	3.27	2.68
Pa	11.63	3.90	3.00	4.49	3.83	4.60	3.82
U	9.31	2.60	1.51	2.46	1.78	2.81	2.00
Np	10.31	2.90	1.84	3.63	2.82	3.73	2.80
Pu	11.89	3.77	2.54	4.49	3.53	4.60	3.54
Am	12.87	4.65	3.28	5.40	4.33	5.45	4.24
Cm	14.09	5.51	4.00	6.25	5.04	6.34	4.99
Bk	15.50	6.32	4.63	7.10	5.73	7.22	5.70
Cf	16.68	7.14	5.29	7.89	6.38	8.07	6.39
Es	18.10	7.99	5.97	8.85	7.18	8.90	7.05
Fm	18.78	8.77	6.57	9.66	7.83	9.70	7.68
Md	19.91	9.55	7.14	10.45	8.43	10.50	8.28
No	21.0	10.29	7.68	11.20	9.00	11.27	8.86
Lr	22.13	10.95	8.12	11.85	9.45	12.03	9.42

TABLE IV: Calculated and Experimental Averaged Bond Energies (in kcal mol^{-1}) for MX$_4$ (M = Th and U; X = F, Cl, Br, and I)^a

	$D(\text{M–X})^{\text{NR}\,b}$	$D(\text{M–X})^{\text{FO}\,c}$	$D(\text{M–X})^{\text{QR}\,d}$	exptl^e
ThF$_4$	176.8	151.4	164.2	159.0
ThCl$_4$	131.1	106.9	112.5	122.5
ThBr$_4$	116.1	91.6	98.1	108.0
ThI$_4$	90.9	72.6	91.2	88.7
UF$_4$	148.5	138.1	154.9	146.3
UCl$_4$	98.5	82.2	98.9	109.4
UBr$_4$	92.7	73.8	92.2	94.7
UI$_4$	78.5	55.6	81.5	75.5

^{a} The M–X bond distances were optimized. ^{b} From nonrelativistic calculations based on eq 21a. ^{c} From first-order relativistic calculations based on eq 21a and E^1 of eq 17. ^{d} From quasi-relativistic calculations based on eq 21b. ^{e} Experimental bond energies from ref 27.

principal valence levels for the third transition series are 6s and 5d, and we depict in Figure 1 the relativistic corrections to the 6s orbital energies as calculated by FO, QR, and DS. It follows from Figure 1 that the relativistic corrections from QR consistently are in better accord with the DS results than the relativistic corrections calculated by FO, in particular toward the end of the series. The 5d valence shell on the other hand is treated adequately by either FO or QR as illustrated in Table I in the case of mercury.

The posttransition series Tl to Rn with $Z = 81–86$ has 6s and 6p orbitals in its valence shell. It follows from Figure 2 that relativistic corrections to the 6s orbitals are reasonably represented by QR, whereas the corresponding values calculated by FO differ considerably from DS results. Thus, the trend observed in the third transition series is seen to have been enhanced further through the posttransition series. The QR method is further seen in Table II to perform better than FO for the $6p_{1/2}$ and $6p_{3/2}$ orbital energies through the posttransition series. The difference between QR and FO is particularly notable for the $6p_{1/2}$ component.

The primary valence shell among the actinides (Th–Lr) with $Z = 90–103$ includes the 6d, 5f, and 7s levels. However, recent calculations have indicated that 6s and 6p are of importance for the bonding in actinide complexes as well.[34–37] The differences between FO, QR, and DS orbital energies for the 6s, $6p_{1/2}$, and $6p_{3/2}$ levels through the actinide series are well represented by the results given in Table I for uranium. Thus orbital energies calculated by the QR method present for both 6s and 6p a closer fit to the DS results than the corresponding energies from FO calculations, just as in the case of the posttransition series. We note, however, that the relativistic corrections to the orbital energies of 6s and 6p are substantial ($\sim$10 eV) for the actinides, and that even QR have notable discrepancies from DS. It is thus clear that the 6s and 6p levels among the actinides are on the border of what one can treat with confidence within the quasi-relativistic approach.

The $5f_{5/2}$ and $5f_{7/2}$ orbital energies for the actinide series are given in Table III. It is clear that the QR method performs better than the FO method with regard to both f-components, and this is also the case for $7s_{1/2}$ as illustrated in the case of U in Table I. It should finally be mentioned that the energies of the 6d

components are calculated accurately by either FO or QR (see results for U in Table I).

The massive collection of data presented in this section would indicate that the quasi-relativistic method and the first-order relativistic approach are equally adequate for the valence levels of light elements up to $Z \sim 70$. The quasi-relativistic method seems, however, to provide better estimates of the orbital energies for the valence levels of heavier elements with $Z > 72$.

V. Molecular Calculations

A. Bond Energies in MCl$_4$ (M = Ti, Zr, and Hf) and MX$_4$ (M = Th, U; X = F, Cl, Br, and I). We have in previous studies analyzed the influence of relativity on metal–ligand[8,11f–i,12] and metal–metal[8,11e] bonds in transition-metal compounds. It was demonstrated in these studies that the relativistic approach based on first-order perturbation theory could reproduce the observed periodic trends within a triad of transition metals adequately. However, an extension of the first-order theory to actinides did not meet with the same degree of success (see later). The inadequacy of the simple first-order theory in actinides, in which relativistic effects are much more important than in transition metals (see section IV), can be explained by the lack of higher order relativistic corrections (in α^2) to either the Hamiltonian or the density or both. It was shown in the last section that the quasi-relativistic method, in which only higher order corrections to the density are included, provided atomic orbital energies in good accord with fully relativistic DS calculations on actinides. We shall here evaluate the same quasi-relativistic approach in connection with calculations on actinide–ligand bond energies.

The thermochemistry of actinide compounds is somewhat limited. However, accurate average M–X bond energies[27] are known for the series of MX$_4$ tetrahalides with M = Th, U and X = F, Cl, Br, I. Calculated averaged bond energies for the MX$_4$ systems are given in Table IV. The calculations are based on the nonrelativistic HFS method ($D(\text{M–X})^{\text{NR}}$) and the relativistic first-order approach ($D(\text{M–X})^{\text{FO}}$) as well as the quasi-relativistic approximation ($D(\text{M–X})^{\text{QR}}$). The experimental[27] averaged bond energies are also included in Table IV for comparison.

The first-order relativistic corrections to the nonrelativistic M–X bond energies $D(\text{M–X})^{\text{NR}}$ are in all cases seen to be negative, that is, $D(\text{M–X})^{\text{FO}} - D(\text{M–X})^{\text{NR}} < 0$. Thus relativistic effects will to first order destabilize the M–X bond. This is a typical[8] situation for predominantly ionic bonds established by transfer of charge from s-type (and to a lesser extent p-type) metal orbitals to orbitals on the more electronegative ligands. The destabilization can be explained in simple terms by recalling that relativity will lower the energy of the s-type donor orbitals on the metals (see section IV) and thus reduce the gain in energy from the density transfer. It follows from Table IV that the M–X bond energies $D(\text{M–X})^{\text{NR}}$ from first-order theory in general are too small in comparison with experimental values.

The first-order relativistic correction to the total energy depends according to eq 17 on the relativistic operator h^1 and the non-

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TABLE V: Calculated and Experimental Bond Energies (in kcal mol^{-1}) for MCl$_4$ (M = Ti, Zr, and Hf) and Cl$_3$MR (M = Ti, Zr, and HF; R = H and CH$_3$)^a

	D(M–X)$^{NR\,b}$	D(M–X)$^{FO\,c}$	D(M–X)$^{QR\,d}$	exptl^a
TiCl$_4$	98.6	98.3	98.1	102.8
TiCl$_3$H^f	60.0	g	g	
TiCl$_3$CH$_3$^{f}	64.0	g	g	
ZrCl$_4$	108.2	107.0	106.4	117.0
ZrCl$_3$H^f	71.1	g	g	
ZrCl$_3$CH$_3$^{f}	74.0	g	g	
HfCl$_4$	115.2	109.1	112.4	118.3
HfCl$_3$H	74.3	75.0	76.1	
HfCl$_3$CH$_3$	77.4	78.1	79.6	

^{a} The M–X bond distances were taken from ref 31a. ^{b} From nonrelativistic calculations based on eq 21a. ^{c} From first-order relativistic calculations based on eq 21a and E^1 of eq 17. ^{d} From quasi-relativistic calculations based on eq 21b. ^{e} Experimental bond energies from ref 27. ^{f} Calculated bond energies from ref 31a. ^{g} Relativistic correction less than 0.4 kcal mol^{-1}.

relativistic density ρ^0. The bond energy D(M–X)^{FO} as a consequence does not incorporate any contributions from changes in the electronic density induced by relativity. Such changes are, on the other hand, incorporated into the quasi-relativistic bond energies D(M–X)^{QR}, as the total energy expression for the quasi-relativistic method, according to eq 20, contains contributions from the change in density to all orders of α^2, at least in an approximate way. It follows from Table IV that the bond energies calculated by the quasi-relativistic method are larger than the bond energies from the first-order theory. Thus, the change in density induced by relativity is seen to have a stabilizing influence on the M–X bond, and the D(M–X)^{QR} values are further found in all cases to be in better agreement with experimental data than the D(M–X)^{FO} values. In fact, the absolute mean deviation for the calculated bond energies is 6.9 kcal mol^{-1} for the quasi-relativistic method as opposed to 16.5 kcal mol^{-1} for the first-order theory.

The change in density from relativistic effects has been studied previously.[28] It involves, in the case of ionic bonds, a reduction in the transfer of charge from the s-type metal orbitals to the np ligand orbitals, in response to the relativistic stabilization of the s-type metal levels. This response is, as already mentioned, not incorporated into the bond energy D(M–X)^{FO} from first-order theory.

We give for the sake of comparison in Table V calculated and experimental M–Cl bond energies for the MCl$_4$ (M = Ti, Zr, and Hf) systems, isoelectronic to ThCl$_4$. It follows from Table V that relativity has a minor influence on the M–Cl bond energies in the three transition-metal complexes MCl$_4$ (M = Ti, Zr, and Hf), even for the 5d-homologue. Further, the relativistic corrections are comparable for FO and QR, although it can be argued that D(M–X)^{QR} is closer to experiment than D(M–X)^{FO} for HfCl$_4$.

B. The Strengths of Actinide–Hydrogen and Actinide–Alkyl Bonds in Organoactinides. The organometallic chemistry of actinides is currently under intense scrutiny.[13b] Of special interest[27] has been the strengths of the actinide–hydrogen and actinide–alkyl bonds. The making and breaking of M–R bonds (R = H, alkyl; M = transition metals or f-block elements) pervades most of the elementary reaction steps in organometallic chemistry. Thus, a knowledge of M–R bond energies would in many cases allow for a more rational approach to the synthesis of organometallics based on quantitative estimates of reaction enthalpies. Of particular importance in this respect are the relative strengths[29a] of the M–H and M–alkyl bonds. The relative strength of the M–H and M–alkyl bonds has important implications[30] for the easy by which ligands can insert into the M–H and M–alkyl bonds as well as the facility by which H$_2$ can add oxidatively to a metal center in

TABLE VI: Calculated and Experimental Averaged Bond Energies (in kcal mol^{-1}) for Cl$_3$MR (M = Th and U; R = H, CH$_3$)^a
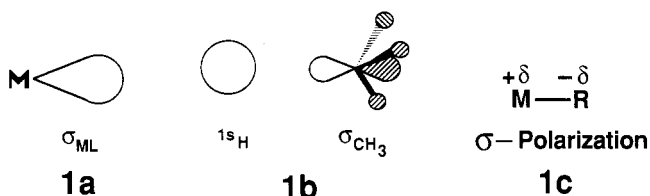
	D(M–X)$^{NR\,b}$	D(M–X)$^{FO\,c}$	D(M–X)$^{QR\,d}$	exptl^e
Cl$_3$ThH	30.1	58.1	76.0	~80
Cl$_3$ThCH$_3$	35.8	59.6	79.8	~80
Cl$_3$UH	10.5	29.3	70.1	76.4
Cl$_3$UCH$_3$	16.8	38.6	72.2	72.4

^{a} The M–R bond distances were optimized. ^{b} From nonrelativistic calculations based on eq 21a. ^{c} From first-order relativistic calculations based on eq 21a and E^1 of eq 17. ^{d} From quasi-relativistic calculations based on eq 21b. ^{e} Experimental bond energies from ref 27 correspond to Cp$_2$MClR systems.

comparison to alkyl–H and alkyl–alkyl bonds. Experimental[27,29] M–R bond energies are only known for a few metal centers.

We have recently[11g,31] studied and rationalized the trend in the relative strengths of M–H and M–alkyl bonds among transition metals. It was found in these studies that M–CH$_3$ bonds are weaker than the corresponding M–H bonds (by some 15 kcal mol^{-1}) for late to middle transition metals,[11g,31a] whereas the two types of bonds are of equal strengths in early transition metals[31b] as shown in Table V for the Cl$_3$MR systems with M = Ti, Zr, and Hf. We shall here extend the study of actinides by investigating Cl$_3$ThR, isoelectronic to Cl$_3$MR (M = Ti, Zr, and Hf), as well as the related Cl$_3$UR system. The M–R bond energies are not available for Cl$_3$MR (M = Th, U). However, Marks[27] et al. have measured D(M–R) in the related Cl(Cp)$_2$MR systems (Cp = cyclopentadienyl). The bond energies due to Marks[27] et al. are displayed in Table VI along with the calculated bond energies for Cl$_3$MR (M = Th, U).

The major component in the bond between Cl$_3$M and R stems from the covalent interaction between a singly occupied orbital (**1a**) on Cl$_3$M and a singly occupied orbital (**1b**) on R (1s$_H$ or σ_{CH_3}). The predominant contribution to **1a** comes in the non-

relativistic case from the 5f$_z$ orbital on Th or U. The nonrelativistic bond energies D(M–R)^{NR} are further seen to be rather small in comparison to the experimental values given in Table VI.

The first-order relativistic correction to the energy of a covalent bond is stabilizing for reasons given in ref 8, and this i also seen to be the case for Cl$_3$MR, although the bond is somewhat polarized (**1c**), with $\delta \sim 0.25$). The first-order corrections are nevertheless too small to bring the calculated values in line with experiment, in particular in the case of the Cl$_3$UR systems (see D(M–X)^{FO} of Table VI).

The inclusion of higher order relativistic corrections to the density by the quasi-relativistic method has important implications for the orbital **1a**, the interaction between **1a** and **1b**, and the M–R bond strength. Thus inclusion of relativistic effects will deplete (or nearly eliminate) the dominating contributions to **1a** from 5f$_z$, as relativity raises the energy of the f-orbitals (see Table I). The orbital **1a** is instead in the quasi-relativistic calculations composed

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of d_{z^2} and s-orbitals on the metal center in a manner quite analogous to that found from nonrelativistic calculations[31a] on the corresponding singly occupied orbital **1a** in Cl_3M with M = Ti, Zr, and Hf. The composition of **1a** from the quasi-relativistic calculation on Cl_3Th and Cl_3U allows for a stronger interaction between **1a** and **1b**, and we find that $D(M-R)^{QR}$ for all systems in Table VI is larger than the corresponding $D(M-R)^{FO}$ value. In fact, the bond energies calculated by the quasi-relativistic method are seen to be in close agreement with the experimental bond energies given in Table VI. Further, the quasi-relativistic calculations on Cl_3ThR and Cl_3UR (Table VI) would indicate that actinides, as is the case for early transition metals (Table V), form bonds to hydrogen and alkyls of nearly equal strength.

VI. Concluding Remarks

The calculation of the first-order relativistic corrections to bond energies by perturbation theory is based on the nonrelativistic wave function (or density matrix) according to eq 17, and energy corrections due to changes ($\Delta\rho^R$) in the density matrix induced by relativity enters only to second or higher orders in α^2. We have shown in the present and earlier studies[8,11,12] that the first-order approach is adequate for calculations of bond energies in compounds containing elements as heavy as gold with $Z = 79$.

The first-order approach is on the other hand not adequate for the heavier actinides where relativistic effects are larger and $\Delta\rho^R$ as a consequence sizable. In particular, we have found that the contributions to the density from f-type and s-type actinide orbitals are changed considerably by relativity. The contributions to the energy from $\Delta\rho^R$ up to the *n*th order in α^2 can in principle be taken into account by resorting to *n*th-order relativistic perturbation theory based on a Foldy–Wouthuysen transformed Dirac Hamiltonian in which terms up to order *n* are retained [for a discussion of divergencies and δ-function contributions see ref 38].

In the quasi-relativistic approach presented here, relativistic corrections ($\Delta\rho^R_{val}$) to the valence density are evaluated variationally to all orders with respect to the first-order Foldy–Wouthuysen transformed Dirac Hamiltonian, whereas the influence from higher order terms in the same Hamiltonian are neglected. Calculations on atomic orbital energies for the valence shells of heavy elements indicate that the quasi-relativistic method provides results in better accord with fully relativistic Dirac–Slater results than the first-order theory. Bond energies from quasi-relativistic calculations are further in better agreement with experiment than bond energies based on first-order theory, in the case of actinide compounds.

The External Heavy Atom Effect: Photophysics of (Dimethylamino)benzonitrile in Cryogenic Rare Gas Matrices

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We have investigated the effects of rare gas external heavy atoms on rate constants of spin-forbidden processes of (dimethylamino)benzonitrile isolated in cryogenic matrices by means of steady-state and time-resolved emission spectroscopy. We interpret the dramatic increase in the phosphorescence yield and the decreases in the fluorescence yield and lifetime and the phosphorescence lifetime in the heavy atom matrices of krypton and xenon in terms of a model in which the rate constant for phosphorescence increases 300-fold in xenon compared to argon, while the rate constants for intersystem crossing to the triplet state and nonradiative relaxation from the triplet state increase by factors of less than 5. Measurements in argon matrices doped with heavy atoms indicate that even one heavy atom neighbor has a significant effect on both singlet and triplet lifetimes. We include higher resolution (up to 0.1 nm) emission spectra of (dimethylamino)benzonitrile detailing vibrational structure which has not previously been observed in the condensed phase. Comparison of the vibrational spacings with a matrix FTIR spectrum indicates that there is distortion of the aromatic ring in the S_1 state, while the shifts in the 0–0 transitions in acetonitrile matrix indicate that the S_1 state is somewhat more polar than either the S_0 or T_1 states.

Introduction

Atoms of high nuclear charge are known to increase rates of spin-forbidden processes, both as a component of the solvent (the external heavy atom effect) and as substituents on the molecule of interest itself (the internal heavy atom effect).[1] Previously, we demonstrated that branching ratios of photochemical reactions in cryogenic rare gas matrices of argon[2] or krypton[3] can be altered by directing reactants to the triplet state with a heavy atom matrix such as xenon. This work is aimed at quantifying the effects of rare gas external heavy atoms on rates of spin-forbidden processes, by examining the photophysics of (dimethylamino)benzonitrile (DMABN) in argon, krypton, and xenon matrices. The high intensity and well-resolved features of its fluorescence and phosphorescence make it a suitable subject for a study of the external heavy atom effect.

DMABN
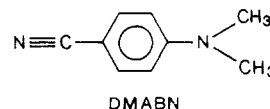
Heavy atom effects on fluorescence and phosphorescence yields (Φ_f and Φ_p, respectively) and on phosphorescence lifetimes[4] (τ_T) have been observed before, but few studies have attempted to determine the effects on individual rate constants. We have measured relative fluorescence and phosphorescence yields and singlet and triplet lifetimes of DMABN isolated in argon, krypton, and xenon, as well as singlet and triplet lifetimes in mixed ar-

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