# Relativistic Effects and Pseudopotentials

1.1 Relativistic effects - Introduction

Even if the correlation energy is known precisely (corresponding to the exact solution of the non-relativistic Schrödinger equation), the calculated total energy would **_not_ equal the real (experimental) energy** of atoms and molecules (See Figure 1). This difference arises from relativistic effects, which increase with the **4th power of the nuclear charge (Z^4) and for the valence electrons, roughly with the 2nd power**. Thus, relativistic effects can be neglected in most cases for lighter atoms, but *have* to be included when dealing with heavy elements.

Figure 1   Correlation energy and relativistic correction
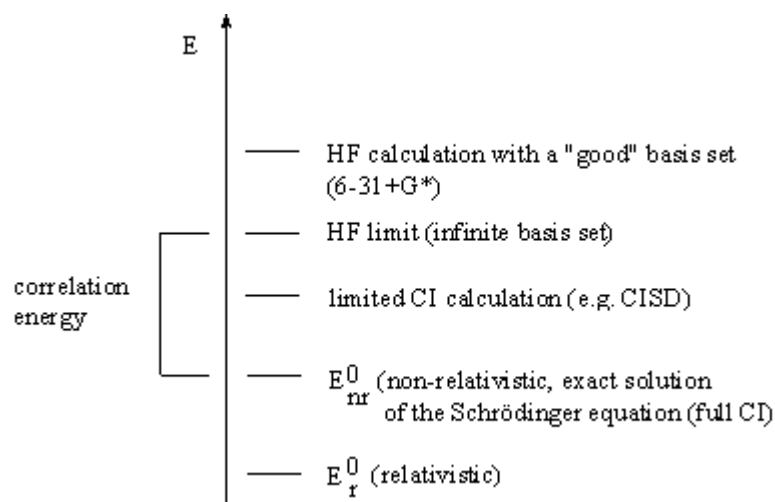
In **non-relativistic quantum mechanics**, the velocity of light can be assumed to be infinite (**$c = \yen$**), so that any finite velocity of particles is very small and the mass of the particle can be approximated by its rest mass (**$m = m_0$**).[1] For most measurements on the lighter elements in the periodic table, non-relativistic quantum mechanics is sufficient, since the velocity of an electron is small compared to the speed of light. For the heavier elements in the periodic table (Au, Hg, Pb, Tl ...etc.) the picture is entirely different. As an example of the considerable influence of relativistic effects, the radial expansion of the **6s orbital of the Cesium atom is reduced by 10%, due to these effects**.[2,3]

As a result for the heavy atoms, the inner electrons attain such high velocities comparable to that of light that non-relativistic quantum mechanics is far from adequate. The difference between non-relativistic results and relativistic results stems from the "true" velocity of light. We can define relativistic effects, in general, as the difference in the results obtained with the true velocity of light and infinite velocity of light. Furthermore, relativistic effects can be divided into a number of categories such as **the mass-velocity correction, Darwin correction, spin-orbit correction, spin-spin interaction, Breit interaction etc**.

The importance of relativistic effects in chemistry has only been fully recognized since the seventies.[4] For heavy elements (from Cu, in any case from Ag on) relativistic effects should be included when performing *ab initio* calculations. Very precise calculations, however, have shown that already for H_2^+ and H_2, relativistic effects contribute to the total energy (e.g. the relativistic contribution to the bond energy for H_2 is -1.43 cal/mol).[5,6,7]

1.2 Kinematic Effects

The mass-velocity correction is the correction **to the kinetic energy of the electron** arising from the variation of its mass with velocity. The relativistic mass increase ($\Delta m = m - m_0$), as a function of the velocity of a moving particle, is given by (special theory of relativity):

$$m = \frac{m_0}{\sqrt{1 - \left(\dfrac{v}{c}\right)^2}}.$$

As the mass of an electron is correlated with its kinetic energy and therefore, with its distance to the nucleus, the mass-velocity effects causes an increased kinetic energy leading to a shorter electron-nucleus distance and thus, especially inner orbitals "shrink". The conclusion we can draw is that the non-relativistic Hamiltonian (in which only the rest masses occur) underestimates kinetic energies. Relativistic effects which are spin-independent are often called kinematic effects.

1.3 Spin-Orbit-Coupling

As the non-relativistic Hamiltonian is "spinless", it is obvious that no coupling between orbital angular momenta and spin can be considered. The electron, due to its spin possesses a magnetic moment. Further, a magnetic moment is associated with the angular momentum. The coupling is caused by the "spinning" electrons acting as tiny magnets, which interacts with the field caused by its motion around the nucleus. This interaction mathematically corresponds to the summation of both vectors (operators) yielding the total angular momentum J which again is quantized. The magnitude of the spin-orbit splitting caused by this interaction is roughly proportional to Z^4, where Z is the nuclear charge; splittings therefore increase very rapidly down the Periodic Table. Spin-orbit coupling can allow an atom to undergo a transition which would otherwise be forbidden by selection rules, such as transition from a singlet to a triplet state.

The coupling of each individual angular momentum of the electrons yields the (total) angular momentum, L. The coupling of each individual spin angular momentum yields the total spin angular momentum, S. The summation of L and S yields the total angular momentum, J, of an electronic system which is called **LS-** or **Russel-Saunders-coupling**. Here the interactions between electrons dominate, and the magnetic interaction can be thought of as small perturbations. This is a good approximation for light and medium-heavy atoms:

$$L = \ell_1 + \ell_2 + ... \ell_N; \ \ S = s_1 + s_2 + ... s_N \ \ \Rightarrow \ \ J = L + S.$$

For heavy atoms, where the magnetic effects due to the spin are much more important, the *j-j-coupling* must be applied**.** Firstly, the angular momentum, ℓ_i, and the spin angular momentum, s_i, of each individual electron is coupled to give the total individual angular momentum, j_i, of the considered electron. Now all individual total angular momenta of the electrons are summed, yielding the total angular momentum of the entire electronic system:

$$j_i = \ell_i + s_i \ \ \Rightarrow \ \ \ J = j_1 + j_2 + ... j_N = \sum_{i=1}^{N} j_i.$$

The spin-orbit correction arises from strong coupling of the spin of the electrons with the orbital angular momentum. It is often said that coupling of spin and orbital angular momenta mixes the multiplicities of terms, and so, for example, singlet terms acquire some

triplet nature, and vice versa. L and S are then said not to be "good" quantum numbers. This is especially true for the electronic states of heavier atoms which arise from open-shell configurations.

The **Breit interaction**, mentioned in the introduction, is the two-electron counterpart of the spin-orbit interaction. The **Darwin correction** is the characteristic outcome of the Darwin relativistic equation. There does not seem to be a simple physical explanation for this effect. The starting point of most relativistic quantum-mechanical methods is the **Dirac equation**, which is the relativistic analog of the Schrödinger equation:

$$\underline{H}^D \Psi = E \Psi \,,$$

where the $\underline{H}^D$ is the Dirac Hamiltonian for a many-electron atom. For the reader who is interested in the derivation of the Dirac equation and the explicit form of the Dirac Hamiltonian we refer to the literature.

1.4 The Impact of Relativistic Effects

Relativistic effects have a significant influence on the electronic properties of heavy atoms and molecules containing heavy atoms. Let us now look at some of these.

Figure 2 Relativistic vs nonrelativistic energy levels of the Au frontier orbitals.
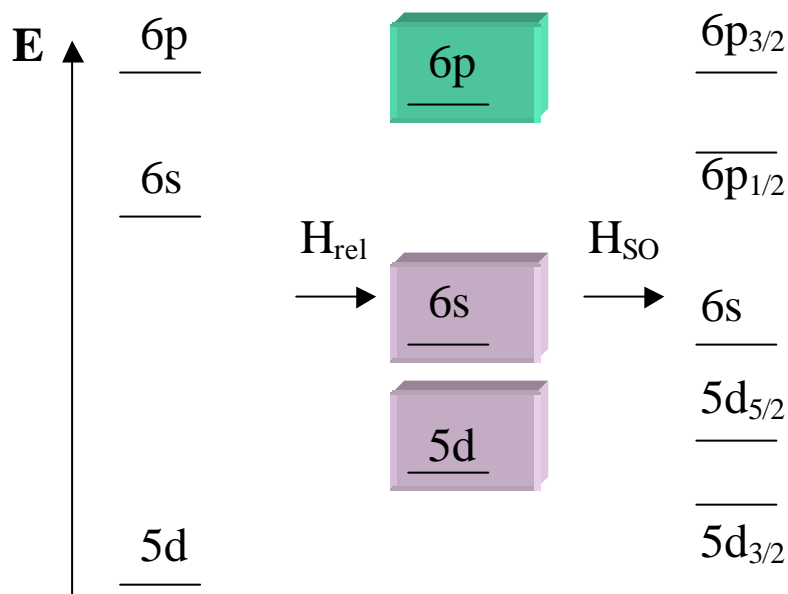
The inner s orbitals are the closest to the nucleus, and thus in the case of heavy atoms experience the high nuclear charge. Hence, the **inner s orbitals "shrink"** as a result of the mass-velocity correction. This, in turn, shrinks the outer s orbitals, as a result of orthogonality. Consequently, the **ionization potential is also raised**. The **p orbitals are also contracted** by mass-velocity corrections, but to a **lesser extent**, since the angular momentum keeps the electrons away from the nuclear regions. However, the **spin-orbit interaction splits the p shells into $p_{1/2}$ and $p_{3/2}$ subshells and expands the $p_{3/2}$**. The net result is that the mass-velocity and spin-orbit interactions tend to cancel for the $p_{3/2}$ shell but are additive for the $p_{1/2}$. The d-orbitals are destabilized (Figure 2)

Spin-orbit interactions alters the spectroscopic properties of molecules containing heavy elements to a considerable extent. Even if a molecule has a closed-shell ground state, the excited states may stem from open-shell electronic configurations, in which case the spin-orbit interaction not only splits the excited states, but mixes different excited states which would not mix in the absence of spin-orbit interaction.

The **Lanthanide contraction** (the decrease of radii from La to Lu) is usually attributed to incomplete shielding of the 4f shell. However, this effect must partly be attributed to relativistic effects. If the non-relativistic Hartree-Fock and Dirac-Fock results are compared, a contribution of about **27% from relativistic effects** is obtained.

1.5 Silver and Gold

Nowhere in the periodic table are the relativistic effects more pronounced than in gold chemistry.[8] The **relativistic contraction** of the 6s shell in the elements Cs (Z = 55) to Fm (Z = 100) shows a **maximum for Au**.[9,10] The contraction increases considerably when the 4f shell is being filled and strikingly when the 5d shell is filled. The pronounced local maximum of the contraction at gold, $(5d)^{10}(6s)^1$, makes Au a unique element, even from this point of view. Figure 1.2 illustrates the nonrelativistic and quasi-relativistic energy levels of the Au frontier orbitals and nicely demonstrates how close the **6s and 5d** orbitals are in energy in the relativistic picture. In agreement with this, **the yellow color of gold can also be attributed to a relativistic effect**. The absorption is attributed to the 5d-to-Fermi level transitions which set in around 2.3 eV in Au. Thus gold reflects the red and yellow and strongly absorbs the blue and violet. The 4d-5s distance of silver is much larger, due to weaker relativistic effects (*NB* The <u>non</u>-relativistic electronic band structures of the two metals are very similar).[11]

The chemical difference between silver and gold has received a great deal of attention during the history of chemistry.[12] It seems to be mainly a relativistic effect.[13] The relativistic effects push the s and p AOs down in energy (effect i) and the d AOs up (effect iii, See Figure 1.2). Moreover, the d AOs suffer a spin-orbit splitting (effect ii). All three effects are much larger for Au than for Ag. The relativistic contraction of the Au 6s shell qualitatively explains the **shorter and stronger covalent bonds**, as well as the **larger ionization potential and electron affinity** of gold.[14,15] The relativistic destabilization of the Au **5d shell qualitatively explains the trivalence of gold**. Besides this energetic effect, the larger radial extension of the 5d shell may also play a role.[16]

1.6 The Aurophilicity of Gold

Though the strong aurophilicity of gold which leads to **cluster formation** may not be described by Lewis-basicity in the classical definition. The formation of clusters containing direct Au-Au interactions falls within the scope of the relativistic discussion in this chapter.

Closed-shell metal cations such as Au^I ($[Xe]4f^{14}5d^{10}$) would normally be expected to repeal one another. By the end of the 1980s, however, there was sufficient crystallographic evidence of attractions between gold(I) cations to lead Schmidbaur to introduce the term "aurophilic attraction" or "aurophilicity".[17] Given that so much of gold chemistry is influenced by relativity, it was natural to inquire as to whether the aurophilic attraction is also a relativistic effect. Görling et al. [18] used Ellis' DV-Xα density functional method to study the electronic structure of a fascinating series of gold cluster compounds, the main-group-element-centered octahedral complexes $[\{(H_3P)Au\}_6X_m]^{m+}$ ($X_1 = B$, $X_2 = C$, $X_3 = N$). These compounds, which may be formally regarded as containing gold(I) cations, feature quite short, "aurophilic" Au-Au distances. Much of the study focused on the role of the gold 5d AOs in **Au-Au bonding**. d-Orbital participation can, of course, be achieved only if the formal d^{10} configuration is broken, e.g. through 6s/5d hybridization. The conclusion was that there is a prominent contribution of the gold 5d AOs to the Au-Au bonding within the cluster, via 6s/5d hybridization in the MOs of a_{1g} symmetry. Furthermore, it was argued that the effect has its origin in the relativistic modification of the gold valence AO energies, which brings the energies of 5d and 6s orbitals into close proximity.

1.7 Mercury

The relativistic contraction of the filled $(6s)^2$ shell of mercury makes it more inert, "almost a rare gas" or "**pseudohelium**". The relativistic interatomic potential V(Hg⋯Hg) is estimated to have only 45% of the depth of the non-relativistic one. To establish definitively why in group 11 cadmium is solid but mercury a liquid at room temperature, detailed calculations are needed. Probably, the explanation is relativistic.

An analogues question would be, why **gallium is a liquid** (mp = 29.8°C despite a high bp = 2205°C)? Perhaps the best answer is that already its crystal structure is very complicated. The alkali metals have both low mp's and low bp's. Ashcroft [19] attributes the complicated crystal structure of gallium to core-core van der Waals interactions which are large compared to the screened Coulomb interactions in the metal.

2.1 The Pseudopotential Method

The **pseudopotential method** is an elegant, approximation which accounts for the most important **relativistic effects** and decreases the **computational costs** of calculation involving heavy elements.[20]

Assuming the validity of the Born-Oppenheimer approximation, the task is to evaluate what happens if the **core electrons** are separated from the **valence electrons**. In this case, the valence electrons can be treated as if they were moving in an **effective potential**, generated by the core electrons (and the nuclei). This procedure (the pseudopotential method) utilizes the fact that only valence electrons take part in chemical bond formation. With this assumption, calculations can be done using the valence basis set only. The cores (inner-shell electrons and the atomic nucleus) of the individual atoms are approximated through a non-local effective potential, the pseudopotential. This potential must satisfy Pauli's principle, which means the valence atomic orbitals (AO) must be orthogonal to the core AOs:

$$\left\langle \Psi^{v} \middle| \Psi^{c} \right\rangle = 0.$$

Separating core and valence electrons leads to an electronic Hamiltonian which describes only the valence electrons $\underline{H}^{v}$. The basis set for orthonormal orbitals belonging to the core subspace must now be determined. This problem is reduced to the minimization of the energy functional:

$$\overline{E}^{v} = \left\langle \Psi^{v} \middle| \underline{H}^{v} \Psi^{v} \right\rangle,$$

The normalized valence orbitals have to satisfy the above mentioned orthogonality condition. The orthogonality condition allows the definition of a projection operator, $\underline{P}$:

$$\underline{P} = \sum_{i} \left| \Psi_{i}^{c} \right\rangle \left\langle \Psi_{i}^{c} \right|,$$

which satisfy the relationship: $\underline{P} \left| \Psi^{c} \right\rangle = \left| \Psi^{c} \right\rangle$. The complementary projection operator is defined as:

$$\underline{Q}\left|\Psi^c\right\rangle = (\underline{1} - \underline{P})\left|\Psi^c\right\rangle = 0.$$

The valence orbitals may be specified with the help of these operators and the **pseudo orbitals** Ψ^p:

$$\left|\Psi^v\right\rangle = \underline{Q}\left|\Psi^p\right\rangle = (\underline{1} - \underline{P})\left|\Psi^p\right\rangle.$$

The pseudoorbitals are not necessarily orthogonal to the core orbitals. The minimization of the energy is then given by:

$$E^v = \left\langle \underline{Q}\Psi^p \left| \underline{H}^v \underline{Q}\Psi^p \right\rangle\right.$$

The orthonormalizing condition for Ψ^v can be introduced by using the method of Lagrange undetermined multipliers:

$$\left\langle \underline{Q}\Psi^p \left| \underline{Q}\Psi^p \right\rangle\right. = 1,$$

As a result of the functional variation, $\delta\Psi^p$, with constraints the following eigenvalue equation results:

$$\underline{H}^{ps}\left|\Psi^p\right\rangle = E^v\left|\Psi^p\right\rangle$$

with pseudo-Hamiltonian ($\underline{V}_R^{GPK}$ = generalized Phillips-Kleinman pseudopotential):

$$\underline{H}^{ps} = \underline{H}^v + \underline{V}_R^{GPK} = \underline{H}^v + (\underline{P}\underline{H}^v\underline{P} - \underline{H}^v\underline{P} - \underline{P}\underline{H}^v + E^v\underline{P}).$$

The form of the pseudo-Hamiltonian is not appropriate, as it contains not only one-electron and two-electron operators, but also multi-electron integrals. For this reason an **effective valence Hamiltonian** is introduced, for which there are different approaches.

The valence pseudoorbitals may be chosen to be in the form of a linear combination of valence and core orbitals:

$$\Psi^p = \Psi^v + \sum_i^{core} a_i^c \Psi_i^c,$$

The a_i^c coefficients can be variationally determined.

The following problems must be considered when solving the pseudopotential equation:[21]

- The *core* orbitals should be known in order to determine an effective valence Hamiltonian

- The pseudopotential is a function of the pseudoorbitals so that an iterative procedure must be used (See SCF method):

  - solution of the HF equation: $\underline{H}^{core} \left| \Psi^c \right\rangle = E^{core} \left| \Psi^c \right\rangle$ for *core* orbitals

  - an estimate of the energy E^v,

  - diagonalization of the matrix of the pseudo-Hamiltonian $\underline{H}^{ps,eff}$ and the

    calculation of the lowest energies E^v by applying the SCF method.

In practice, semiempirical approaches are applied in which the pseudoorbitals and the corresponding pseudopotentials are constructed from the known (experimentally observed or calculated) atomic energy values.

Depending on the analytic form generally three types of pseudopotentials are applied: Local, semi-local and non-local. In practice, semi-local pseudopotentials are used which will be discussed in more detail.[22]

As pointed out before, within the pseudopotential procedure, only the valence electrons, or the electrons in the **(n-1)th shell**, are explicitly considered (in contrast to all-electron calculations). In this case, the electronic Hamiltonian can be reduced to an **atomic valence operator**, $\underline{H}^{val}$ (the indices, i and j, denote only valence electrons!)

$$\underline{H}^{val} = -\frac{1}{2}\sum_{i=1}^{N_v} \Delta_i + \sum_{i=1}^{N_v} \underline{V}(r_i) + \sum_{i<j}^{N_v} \frac{1}{r_{ij}},$$

where $\underline{V}(r_i)$ represents an one-component, **(spin-orbit-averaged) quasi-relativistic pseudopotential**:[23]

$$\underline{V}(r_i) = -\sum_i^{N_v} \frac{Z}{r_i} + \sum_\ell \sum_k A_{\ell k} \exp(-\alpha_{\ell k} r_i^2)\underline{P}_\ell$$

$\underline{P}_\ell$ is the projection operator onto the subspace with angular symmetry ℓ :

$$\underline{P}_\ell = \sum_{m_\ell=1}^{\ell} \left| Y_{\ell,m_\ell} \right\rangle \left\langle Y_{\ell,m_\ell} \right|.$$

The **pseudopotential parameters**, the coefficients, $A_{\ell k}$ and the exponential parameters, $\alpha_{\ell k}$, are adjusted to total-valence energies, derived from numerical all-electron calculations in the following way. Firstly, non-relativistic HF and **quasi-relativistic Wood-Boring (WB)** calculations are carried out for the core system and for **several low-lying neutral and ionic states of the atoms**, by considering all electrons variationally.[24] In the quasi-relativistic calculation, the **mass-velocity term** and the (averaged) **Darwin spin-orbit term** are taken into account, being the major relativistic corrections. A mass-velocity term and a Darwin term are added to the non-relativistic Hartree-Fock operator $\underline{F}_i^{nr}$ for the ith orbital:[25]

$$\left(\underline{F}_i^{nr} + \underline{h}_i^{mv} + \underline{h}_i^{D} \right)\Psi_i = \varepsilon_i \Psi_i.$$

A more detailed description can be found in literature.

The pseudopotentials for atoms can be used for molecules containing heavy atoms. These potentials can easily be implemented in quantum mechanical programs. The pseudopotential approximation is **not exact**. This is especially true when applying atomic pseudopotentials for molecular problems. However, pseudopotential methods can be very effective, e.g. for coordination compounds. They enable the use of extended valence orbital basis sets which, with the limited speed and capacity of existing computers, can lead to results superior to those obtained by *ab initio* calculations with small basis sets.

2.2 A few hints for practical calculations

Some of the simple hints for practical applications of effective core potentials given in the following may appear to be trivial or superuous for some of the readers, but experience during the last years showed that they may be welcome by the more application-oriented ones who are less familiar with the methods. Effective core potentials are usually a good and safe choice when properties related to the valence electron system are to be investigated. It should always be remembered, however, **that the size of the core not only determines the computational effort, but it also inuences the accuracy of the results**. Small-core and medium-core potentials are usually safe to use, whereas the range of large-core potentials is much more limited. In the latter case it might be important to include a **core-core and/or core-nucleus repulsion correction** as well as a **core polarization potential**. It is not a wise decision to simply neglect these terms, e.g., because the CPP (*C*ore *P*olarization *P*seudopotential) is not implemented in GAUSSIAN yet. When using an effective core potential for the first time always do an **atomic test calculation** first, e.g., for the ionization potential or electron affinity, in order to check the correctness of your input and/or the programs library data. Especially in pseudopotential calculations well-known sources of input errors are the $1/r^n$ prefactors used in some parametrizations or the presence/absence of a local potential. It is recommended to use the **valence basis set coming with the effective core potential**, possibly augmented by additional diffuse and polarizations functions. Especially in case of pseudopotentials, where the detailed innermost shape of the pseudoorbitals is essentially arbitrary, it is not recommended to use (contracted) all-electron basis sets or valence basis sets from other potentials, since significant **basis set superposition errors** may result. However, the added diffuse and polarization functions may safely be taken from all-electron or other effective core potential basis sets. When comparing to other all-electron or valence-only calculations use basis sets and correlation treatments of the same quality and make sure that relativistic effects are included at similar levels. Note that in all-electron calculations basis set superposition errors tend to be larger than in valence-only calculations.

2.3 ECP input format

The **PSEUDO** keyword requests that a model potential be substituted for the core electrons. *Gaussian* 98/94 (compared to older versions) supports a new **effective core potential** (ECP) input format (similar to that used by **ExtraBasis**) which is described below. When reading-in pseudopotentials, do not give them the same names as any internally-stored pseudopotentials: **CEP** (Compact Effective Potentials), **CHF**, **LANL1**, **LANL2**, **LP-31**, **SDD** and **SHC**.

ECP input without pseudo keyword:

#hf/**sdd** opt gfinput

blank line

Au-F using pseudopotentials for Au but *NOT* for F (6111,41) basis set

blank line

0,1

Au

F 1 1.9

The **PSEUDO** keyword can be used in connection with the following **option:**

Read Means : Read pseudo-potential data from the input stream.

#HF/GEN PSEUDO=READ gfinput

Effective Core Potential operators are sums of products of polynomial radial functions, Gaussian radial functions and angular momentum projection operators. ECP input therefore specifies which potential to use on each atomic center, and then includes a collection of triplets of:

(coefficient, power of R, exponent)

for each potential for each term in each angular momentum of the ECP. Since only the first few angular momentum components have different terms, the potential is expressed as (1) terms for the general case, typically d or f and higher projection, and (2) the extra terms for each special angular momentum. Thus for an LP-31G potential, which includes special s and p projected terms, the input includes the general (d and higher) term, the s-d term (i.e., what to add to the general term to make the s component) and the p-d term.

All ECP input is free-format. Each block is introduced by a line containing the center numbers (from the molecule specification) and/or atomic symbols, specifying the atoms and/or atoms types to which it applies The list ends with a value of 0.

The pseudo-potential for those centers/atoms follows:

Name,Max,Icore

Name of the potential, maximum angular momentum of the potential (i.e., 2 if there are special s and projections, 3 if there are s, p, and d projections), and number of core electrons replaced by the potential. If *Name* matches the name of a previous potential, that potential is reused and no further input other than the terminator line (see below) is required.

For each component (*I*=1 to *Max*) of the current potential, a group of terms is read, containing the following information:

Title

A description of the block, not otherwise used.

Nterm

Number of terms in the block.

NPower,Expon,Coef

Power of R, exponent, and coefficient for each of the *NTerm* terms. *NPower* includes the R^2 Jacobian factor.

2.4 Pseudopotentials of the Stuttgart/(Dresden) Köln group

The energy-consistent pseudopotentials of the Stuttgart/Köln group are semi-local pseudopotentials adjusted to reproduce atomic valence-energy spectra. The adjustment of the pseudopotential parameters has been done in fully numerical calculations, valence basis sets have been generated a-posteriori via energy optimization. The complete set of potentials includes one-component (non-relativistic and scalar-relativistic) effective-core potentials (ECP), spin-orbit (SO) and core-polarization potentials (CPP).

In **Pseudo** input, keywords for these ECP's are of the form **ECP*XYn*** where *n* is the number of core electrons which are replaced by the pseudopotential and *X* denotes the reference system used for generating the pseudopotential (**S** for a single-valence-electron ion or **M** for a neutral atom).

Y specifies the theoretical level of the reference data: **HF** for Hartree-Fock, **WB** for Wood-Boring quasi-relativistic and **DF** for Dirac-Fock relativistic. For one- or two-valence electron atoms **SDF** is a good choice; otherwise **MWB** or **MDF** is recommended (although for small atoms or for the consideration of relativistic effects, the corresponding **SHF** and **MHF** pseudopotentials may be useful).

For light atoms, or for the discussion of relativistic effects, the corresponding SHF, MHF pseudopotentials may be useful. The same keyword applies to the set of pseudopotential parameters and the corresponding optimized valence basis sets.

Keyword in Gaussian for Pseudopotentials and corresponding valence basis sets of the Stuttgart/Köln group

SDD

Requests an effective pseudopotential of the Stuttgart/Köln goup. Let's have a look at a typical **input example for the HI molecule** using an all-electron basis set for hydrogen and a SDD pseudopotential for iodine (or see above the AuF example with ECPs for Au and F).

%kjob l301   *Test job kills program after l301*

#hf/gen **pseudo=read** gfinput

blank line

i-ecp-mwb 4 46 (4 = l's with l = 0,1,2,3; 46 = # core electrons)
blank line

0,1
H
I   1   2.0

blank line

H 0
6-31G(d,p)   *name of the all electron basis set for H*
****
I 0
SDD   *name of valence basis set for iodine*
****

blank line

I 0   *ECPs for the iodine atoms*
SDD   *name*

Output

...
General basis read from cards: (5D, 7F)
 AO basis set in the form of general basis input:
  1 0
 S   3 1.00   0.000000000000
     0.1873113696D+02 0.3349460434D-01
     0.2825394365D+01 0.2347269535D+00
     0.6401216923D+00 0.8137573261D+00
 S   1 1.00   0.000000000000
     0.1612777588D+00 0.1000000000D+01
 P   1 1.00   0.000000000000
     0.1100000000D+01 0.1000000000D+01
 ****
  2 0
 S   3 1.00   0.000000000000
     0.2122765000D+01 0.2063429899D+01
     0.1770481000D+01 -0.2869526473D+01
     0.3130840000D+00 0.1404747074D+01
 S   1 1.00   0.000000000000
     0.1240710000D+00 0.1000000000D+01
 P   3 1.00   0.000000000000
     0.2432887000D+01 0.7732753148D+00
     0.2137249000D+01 -0.1020833156D+01
     0.3145460000D+00 0.1095666871D+01
 P   1 1.00   0.000000000000
     0.1049450000D+00 0.1000000000D+01
 P   1 1.00   0.000000000000
     0.3264100000D-01 0.1000000000D+01
 ****

…

```
================================================================
Pseudopotential Parameters
================================================================
```

Center Number	Atomic Number	Valence Electrons	Angular Momentum	Power of R	Exponent	Coefficient	Coordinates X Y Z
1	1						0.000 0.000 -3.709
			No pseudopotential on this center.				
2	53	7					0.000 0.000 0.069
			G and up	2	1.0000000	0.00000000	
			S - G	2	3.5112000	83.11386300	
				2	1.7556000	5.20187600	
			P - G	2	2.9688000	82.81110900	
				2	1.4844000	3.37968200	
			D - G	2	1.9066000	10.30427700	
				2	0.9533000	7.58803200	
			F - G	2	2.3075000	-21.47793600	

```
================================================================
```
There are   8 symmetry adapted basis functions of A1 symmetry.
There are   0 symmetry adapted basis functions of A2 symmetry.
There are   4 symmetry adapted basis functions of B1 symmetry.
There are   4 symmetry adapted basis functions of B2 symmetry.
Integral buffers will be   262144 words long.
Raffenetti 1 integral format.
Two-electron integral symmetry is turned on.
   16 basis functions,   **26 primitive gaussians**,   16 cartesian basis functions
    4 alpha electrons   **4 beta electrons**
    nuclear repulsion energy   1.8521202291 Hartrees.
...

S – G   l = 0 – k = 1 and l = 0 – k = 2

P – G   l = 1 – k = 1 and l = 1 – k = 2

D – G   l = 2 – k = 1 and l = 2 - k = 2

F – G   l = 3 – k = 1

$$\underline{V}(r_i) = -\sum_{i}^{N_v} \frac{Z}{r_i} + \sum_{\ell} \sum_{k} A_{\ell k} \exp(-\alpha_{\ell k} r_i^2)\underline{P}_\ell$$

How can the pseuodopotential explicitly be incorporated? (See format section).

Input example HI.

%kjob l301

#hf/gen pseudo=read gfinput

i-ecp-mwb 4 46 (4 = l = 0,1,2,3; 46 = # core electrons)

0,1
H
I 1 2.0

H 0
6-31G(d,p)
****
I 0
SDD
****

I   0
I-ECP-mwb   4   46
G POTENTIAL
 1
2   1.00000000   0.00000000
S-G POTENTIAL
 2
2   3.51120000   83.11386300
2   1.75560000   5.20187600
P-G POTENTIAL
 2
2   2.96880000   82.81110900
2   1.48440000   3.37968200
D-G POTENTIAL
 2
2   1.90660000   10.30427700
2   0.95330000   7.58803200
F-G POTENTIAL
 1
2   2.30750000   -21.47793600

These data can easily be obtained from

(i) http://www.emsl.pnl.gov/forms/basisform.html or

(ii) http://www.theochem.uni-stuttgart.de/pseudopotentials/.

The last home page (Prof. Werner, Uni Stuttgart) can truly be recommended.

2.5 (LANL1 and) LANL2 Pseudopotentials

Keyword: LANL1 or LANL2 (do not work without DZ!)

Requests the LANL1/2 potentials: describe the core electrons by the Los Alamos National Laboratory 2 (LANL2) effective core (by Hay and Wadt [26])

#hf/**gen** opt gfinput pseudo=read

blank line

Au-F using pseudopotentials for Au and F

blank line

0,1

Au

F 1 1.9

blank line

```
Au 0
Lanl2DZ                              basis set for Au
****
F 0
6-31G(d)                             basis set for F
****
```

blank line   **ECP for Au**

```
Au 0
Lanl2DZ
```

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