Pseudopotentials $\equiv$ Effective Core Potential (ECP)

\[
\begin{align*}
\text{Si} & \quad 1s^2 \ 2s^2 \ 2p^6 \ 3s^2 \ 3p^2 \\
\text{Cu} & \quad 1s^2 \ 2s^2 \ 2p^6 \ 3s^2 \ 3p^6 \ 3d^{10}4s
\end{align*}
\]

The inner electrons are not evolved in chemistry, and they make the calculations expensive, because their presence requires large basis sets.

<table>
<thead>
<tr>
<th></th>
<th>all-el.</th>
<th>pseudo</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>3s2p1d (14)</td>
<td>2s2p1d</td>
</tr>
<tr>
<td>Si</td>
<td>4s3p1d (18)</td>
<td>2s2p1d</td>
</tr>
<tr>
<td>Cu</td>
<td>5s4p3d1f (39)</td>
<td>3s3p2d</td>
</tr>
</tbody>
</table>

Actually, for an element such as Cu, there are different ways one can do the core-valence split.
Core

I. \(1s^2\ 2s^2\ 2p^6\)

II. \(1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\)

III. \(1s^2\ 2s^2\ 2p^6\ 3s^3\ 3p^6\ 3d^{10}\)

For Cu, I and II give similar quality results, but for other first-row transition metal atoms, I may be preferable to II.

For Cu, III does not work well.

significant error in IP
about a factor of 2 error in \(D_e(Cu_2)\).
The above comments pertain to the use of static ECPs.

Stoll and coworkers have developed polarizable-core ECPs. (In Molpro, but not in G03).

with these, one can do quite well treating Cu as a “one electron atom”;

Obviously, can't be used to describe d⁹ s² excited states.

In GTO-based codes, ECPs are of the form:

\[ U_{ECP}(r) = \sum_i a_i r^{n_i} e^{-\alpha_i r^2} \]

Parameters generally chosen to reproduce orbital energies from all-electron HF or DFT calculations

generally angular momentum dependent
For heavy elements, ECPs are usually chosen to reproduce the results of all-electron relativistic calculations.

⇒ ECP calculations build in relativistic contraction!

NOTE: spin-orbit interactions are also a consequence of relativistic effects.
These would still be needed to be treated explicitly, even if using a relativistic ECP
The adoption of pseudopotentials is even more important for calculations with plane-wave ($e^{ik\cdot r}$) basis set.

$k$ and $r$ are conjugate variables, related by Fourier transfer.

Rapid variations in orbitals at small $r \Rightarrow$ need high $k$.

Basis sets would be prohibitively large without ECPs.