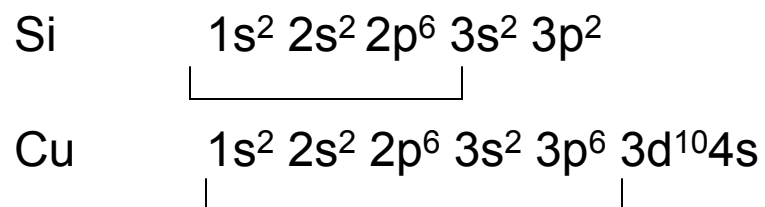


Pseudopotentials \equiv Effective Core Potential (ECP)



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

	<u>all-el.</u>	<u>pseudo</u>	
C	3s2p1d (14)	2s2p1d	} large computational savings
Si	4s3p1d (18)	2s2p1d	
Cu	5s4p3d1f (39)	3s3p2d	

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 $D_e(\text{Cu}_2)$.

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 $d^9 s^2$ 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.
