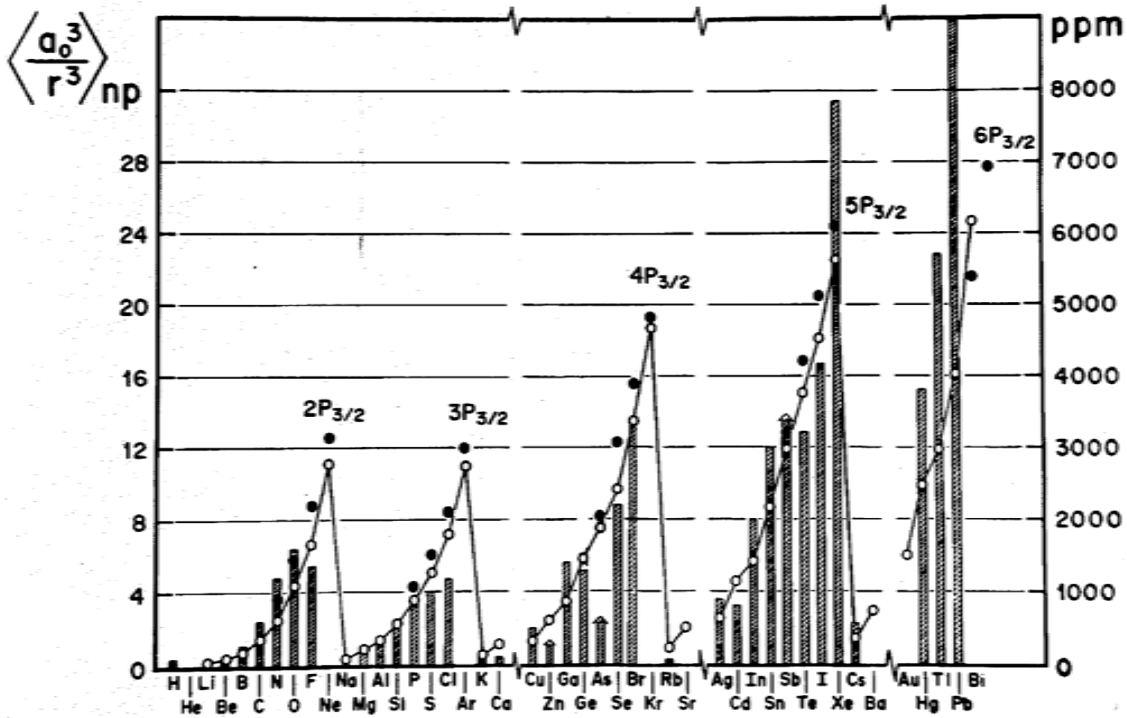
Periodic Table-wide Trends in Chemical Shifts and J coupling



Cynthia J. Jameson

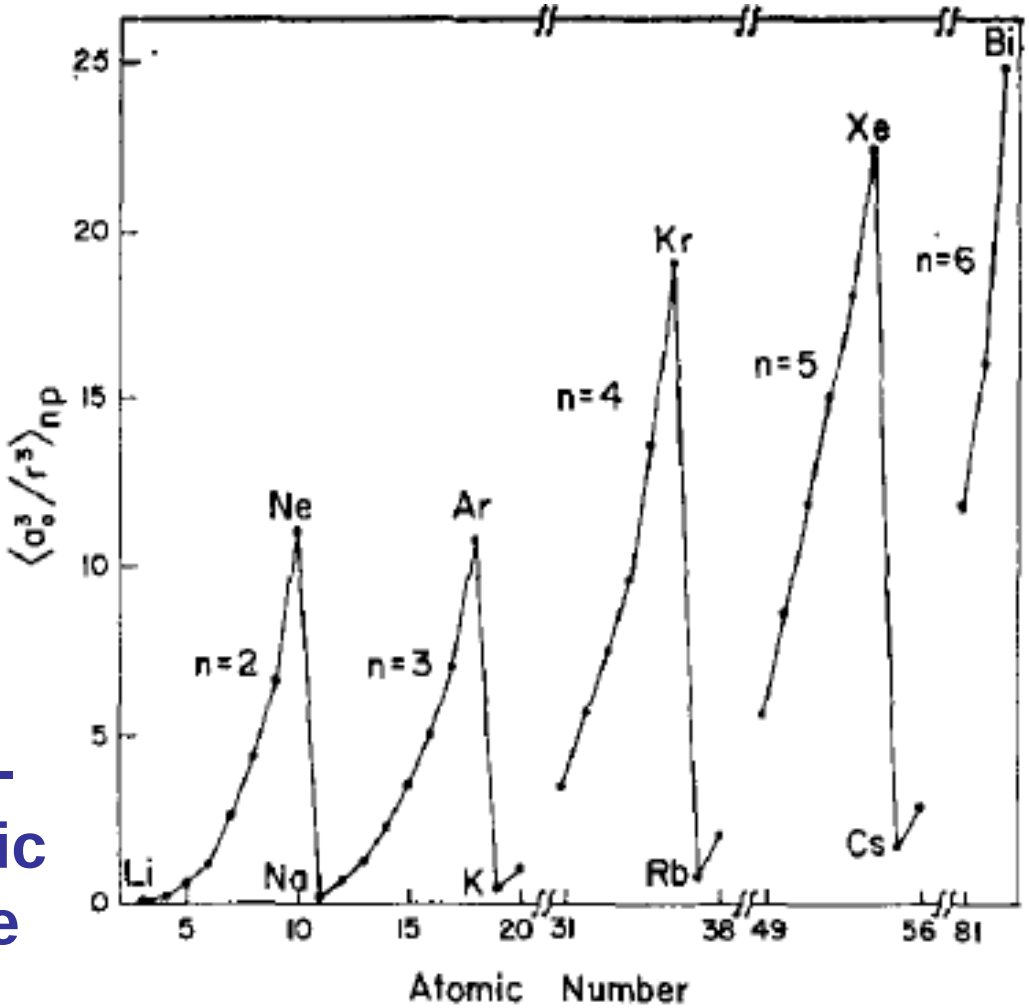
University of Illinois at Chicago

Periodic trends are observed in:

- ranges of chemical shifts of nuclei across the Periodic Table
- chemical shift comparisons for nuclei of same column (group) in analogous compounds
- signs of one-bond reduced J coupling across the Periodic Table
- magnitudes of reduced J coupling across the Periodic Table to the same nucleus in analogous compounds

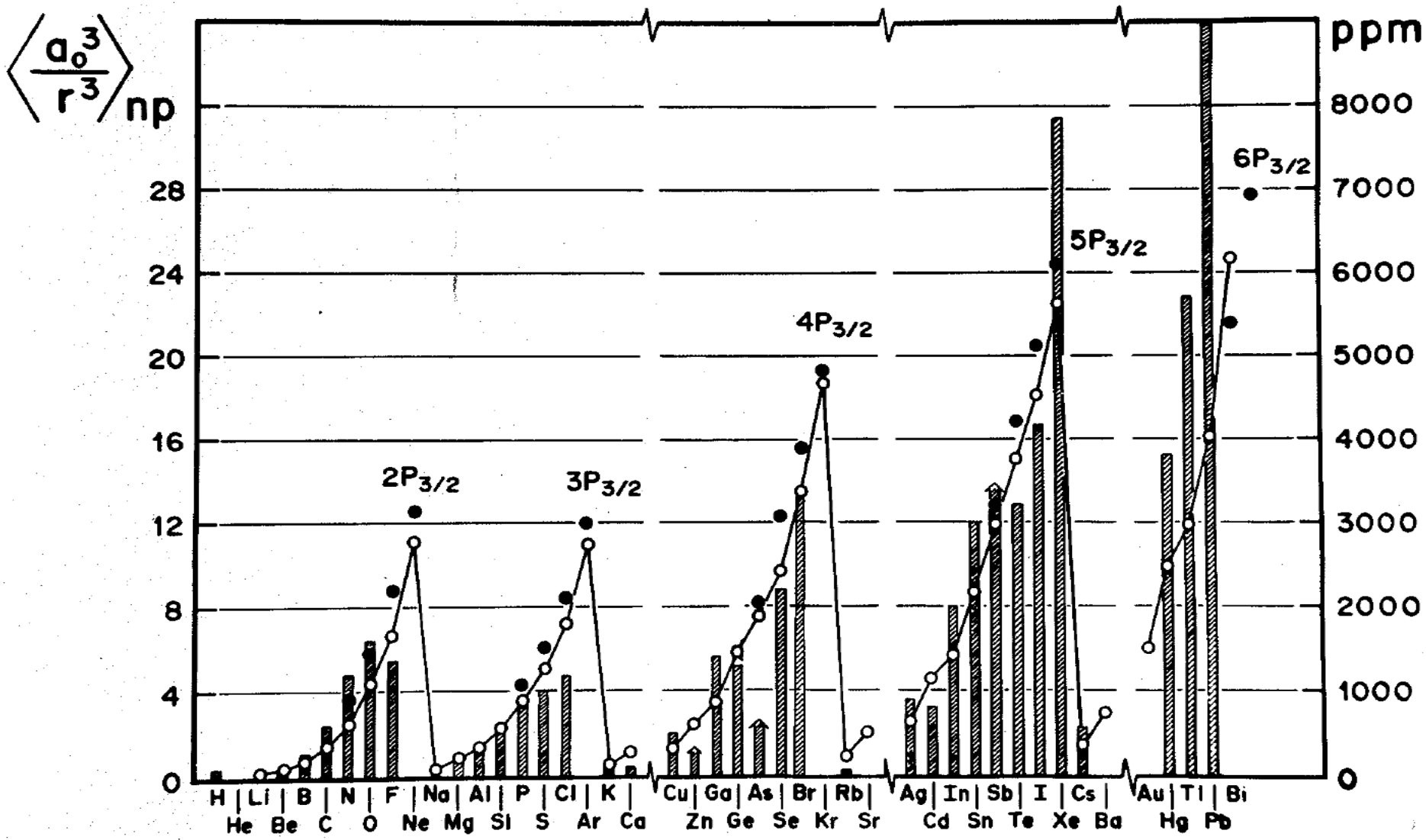
$\langle a_0^3/r^3 \rangle$

Jameson & Gutowsky predicted that the sensitivity of the chemical shifts to changes in the chemical environment would scale according to the characteristic $\langle a_0^3/r^3 \rangle$, which is obtained from the spin-orbit splittings in atomic spectra, for the valence p shell (or d for transition elements) of the free atom in its ground state.



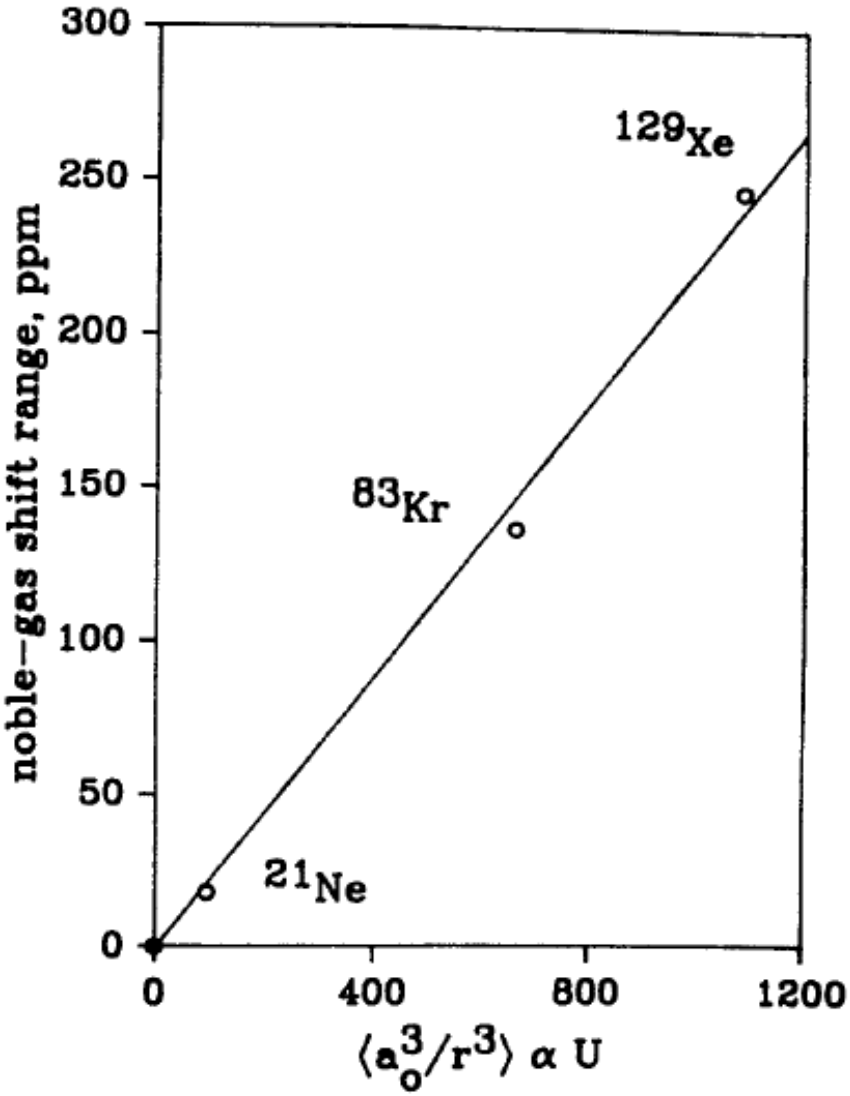
C. J. Jameson & H. S. Gutowsky,
J. Chem. Phys. 40, 1714-1724 (1964)

More than 20 years later, this is clearly demonstrated by the correlation with $\langle a_0^3/r^3 \rangle$ of the ranges of the chemical shifts observed in Periodic Table–wide trends



from C. J. Jameson and J. Mason,
in *Multinuclear NMR*, Plenum, 1987

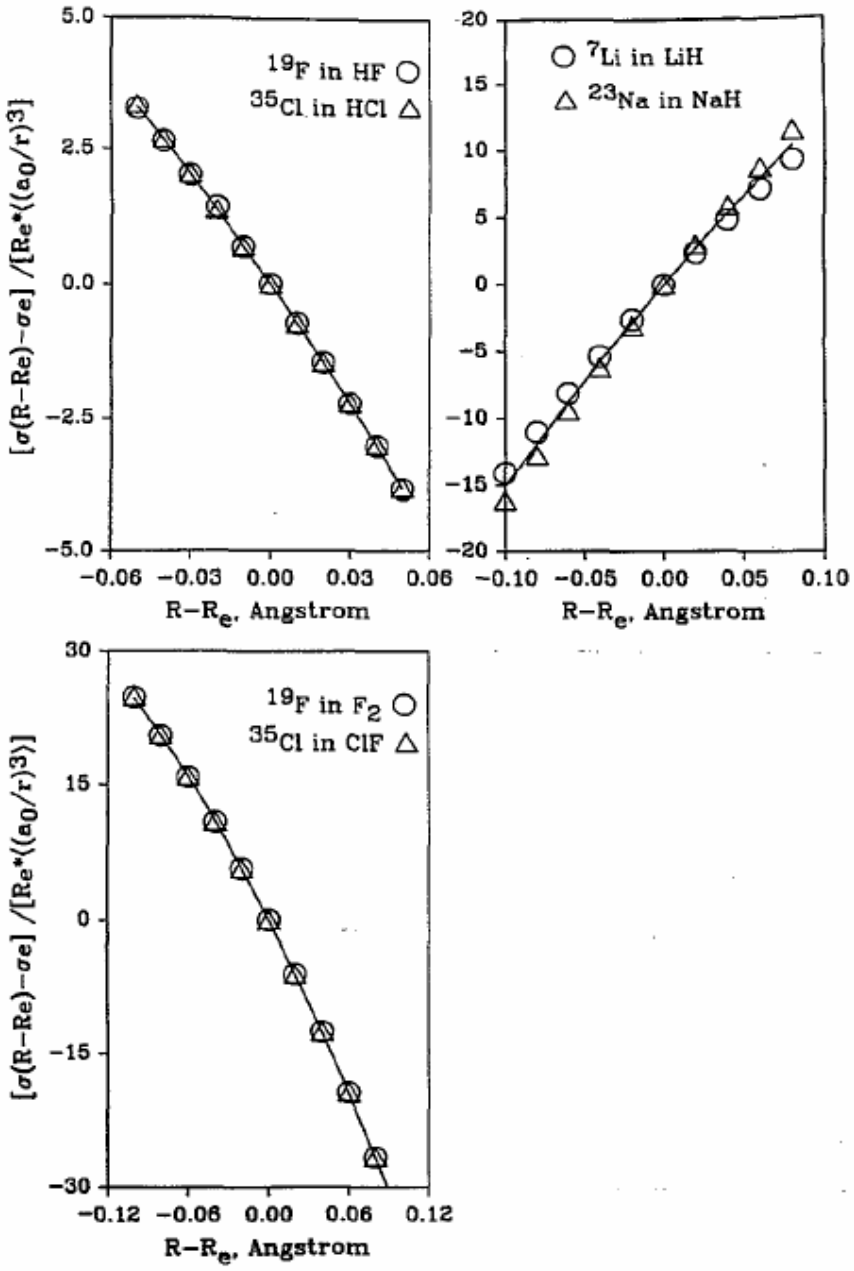
The same $\langle a_0^3/r^3 \rangle$ scaling factor is found in ranges of intermolecular chemical shifts for rare gas atoms



The ranges of gas-to-solution chemical shifts for Ne, Kr, and Xe measured in a common set of organic liquids are compared against the scaling factors.

C. J. Jameson & A. C. de Dios,
J. Chem. Phys. 97, 417-434 (1992)

The **intramolecular shielding surfaces** (shielding vs. bond length) for analogous diatomic molecules scale in the same way, with $R_e\langle a_0^3/r^3\rangle$



C. J. Jameson and A. C. de Dios, The nuclear magnetic shielding as a function of internuclear separation," *J. Chem. Phys*., 98, 2208-2217 (1993)

Trends are also observed in other quantities for nucleus M across the Periodic Table, quantities which depend on derivatives of intramolecular shielding surfaces:

- M isotope shifts upon deuteration
- Temperature dependence of M chemical shifts in the isolated molecule

C. J. Jameson and H. J. Osten,
J. Am. Chem. Soc. 107, 4158-4161 (1985).

Periodicity in spin-spin coupling

Prediction in 1964:

One would expect KMH

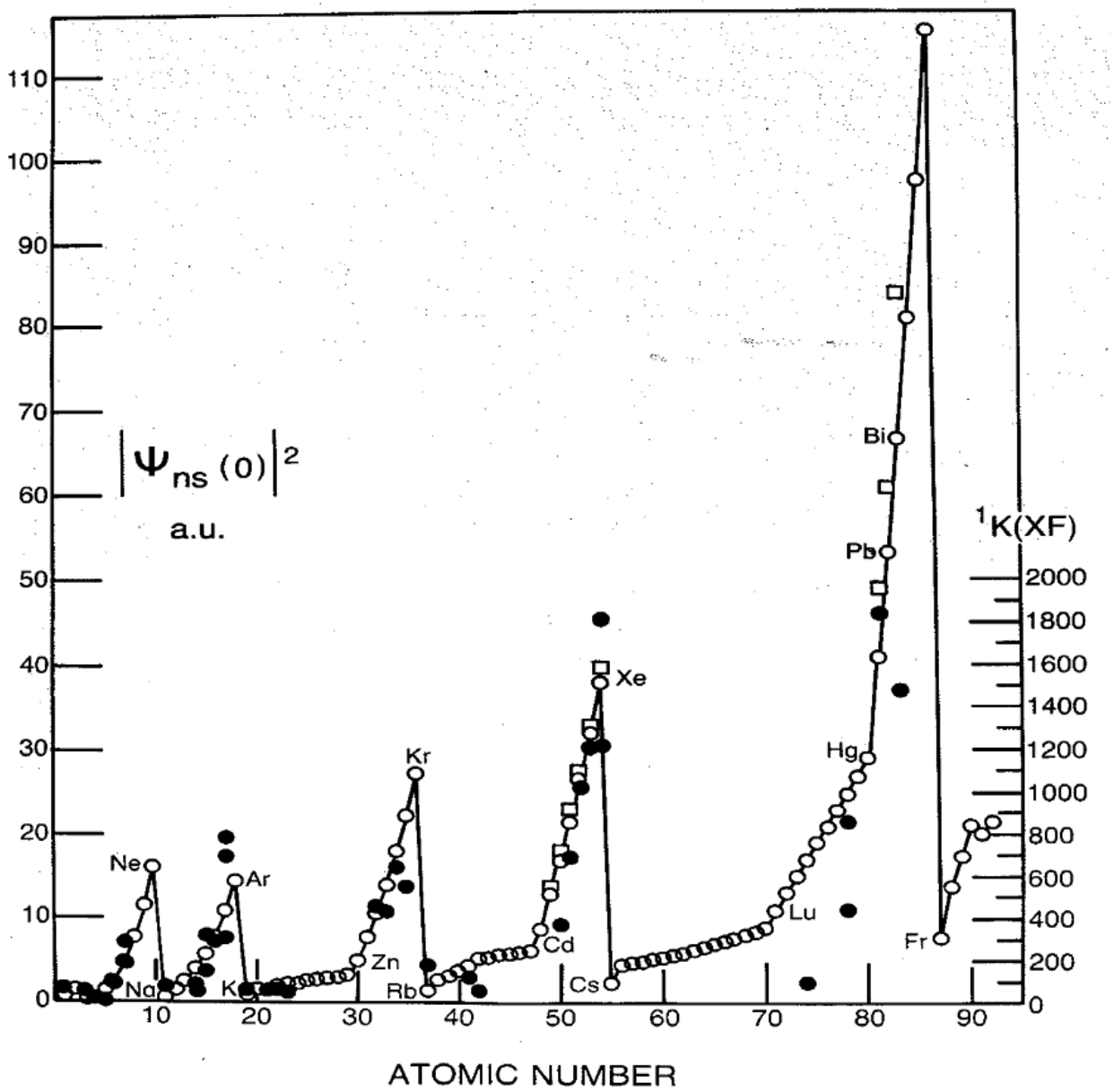
(the reduced coupling constant , $(J_{MH}/\gamma_M\gamma_H)$

to reflect the periodicity in $|\Psi_{ns,\,M}(0)|^2$

for the atoms.

C. J. Jameson & H. S. Gutowsky,
Calculation of chemical shifts. I.
General formulation and the Z dependence
J. Chem. Phys. 40, 1714-1724 (1964)

More than 20 years later, magnitudes of reduced J coupling (•) across the Periodic Table to the same nucleus(^{19}F) in analogous compounds exhibit the same periodicity as $|\Psi_{ns}(0)|^2$ (o)



from C. J. Jameson,
in *Multinuclear NMR*, Plenum, 1987

Sign of one-bond reduced coupling constant K_{MH}

- 1969 prediction of Periodic Table –wide trends based on Fermi contact contribution, & analysis of valence ns shell and core polarization contributions:

  C. J. Jameson and H. S. Gutowsky, Systematic trends in the coupling constants of directly bonded nuclei *J. Chem. Phys.* 51, 2790-2803 (1969)

- experimental trends:

  C. J. Jameson, Theoretical considerations: Spin-spin coupling, in 31P NMR Spectroscopy in Stereochemical Analysis: Organic Compounds and Metal Complexes, J. G. Verkade and L. D. Quin, Eds., Verlag Chemie Intl, 1987, pp. 205-230.

ACKNOWLEDGMENT

The academic environment in H. S. Gutowsky's group back in the early 1960s encouraged insightful discoveries in NMR even in the neophyte Ph.D. student.