Effective Ions-in-Molecule Potentials for Non-Penetrating Rydberg States of Polar Molecules

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Ions-in-molecule, but with polarization terms added.

Electrostatic theories ... do not give satisfactory quantitative agreement with experiment. ... The difficulty is that of taking account of covalent bonding and polarization, which are closely related, but not identical, phenomena."
Leslie E. Orgel in *Transition Metal Chemistry Ligand Field Theory.*

Effective potentials? What about Quantum Defect Theory fitting?

- Interpretation of Rydberg spectroscopic data for polar molecules makes use of effective potentials that include both ionic bonding and polarizability in order to represent electric properties of the ion core. Quantum defect theory (QDT) models the spectrum but effective potentials yield physical properties.
- Convergence properties of multipole + polarization potentials depend on the origin of the expansion. (origin at centers of (charge, dipole, mass, *polarizability*), but there are families of origin-invariant reductions.
- Multipole series are asymptotic. They are most accurate when the terms omitted are minimized by a good choice of origin.
- Atom-centered potentials remove the origin-dependence but are not generally more accurate than single-center expansions. The literature form is not self-consistent. The two forms make different predictions of core properties.
- BaF+ is shown as an example.

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What can Rydberg-land learn from the molecular, non-Rydberg traditions in non-relativistic long-range potentials?

Who created the field?

L. Silberstein (1917!), A. David Buckingham, Jon Applequist, Anthony J. Stone, P. W. Fowler, Madden, George Maroulis, J. Hutson, J. R. Schmidt. T. Oka, van Kranendonk, Gray, H. M. Pickett, ...

Subjects studied in the same framework:

Refraction and scattering of light, the quadrupole paradox, Van der Waals complexes, energy and polarization in ionic crystals, force fields for molecular mechanics, rotational energy transfer.

Connections to Rydberg-land:

Frédéric Merkt, a student of A. D. Buckingham, references T. Oka in a 2014 PRL on long-range dimerization of cold Cs Rydberg atoms. Beautiful.

Not discussed here, assumed to be "well-known":

Papers completely within the atomic or Rydberg traditions. (Wigner, Seaton, Fano, Ch. Jungen, Chris Greene, S. Lundeen, E. Eyler, F. Merkt, …, and RWF)

On offer:
- multi-center potentials accurate to short range,
- complete perturbation theory expansions,
- analysis of convergence properties,
- integration with other fields of chemistry and chemical physics.

Three non-relativistic Born-Oppenheimer effective potentials for a molecular ion in the field of an external point charge

Multipole, single center, expansion of core energy	Truncated two-center potential used by Arif, Jungen, Roche(1997)	Two-center potential with full feedback

$$W(\mathbf{r}) = W^{(0)} + W^{(2)} + W^{(HP)}$$

(0) **electrostatic**,
(2) **linear polarization response** from second order PT,
(HP) **higher order** hyperpolarizability **Cartesian form** depending on values and derivatives of the externally applied potential, as in

$$W^{(2)} = -\frac{1}{2}\alpha_{\alpha\beta}V_{\alpha}V_{\beta} - \frac{1}{3}A_{\alpha,\beta\gamma}V_{\alpha}V_{\beta\gamma} - \cdots$$
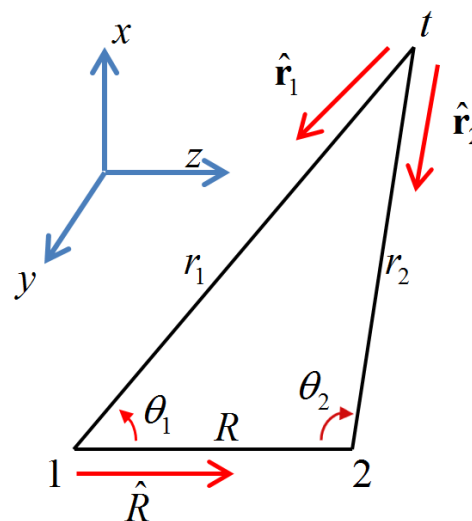
Spherical multipole expansion reduction for **cylindrical symmetry** (NOT Π states, ...)

$$W(\mathbf{r}) = \frac{1}{4\pi\varepsilon_0}\sum_L \frac{C_{L,0}(\theta,0)}{r^{L+1}}Q_L^{\text{eff}}$$

Qeff = (**static – polarization**) terms

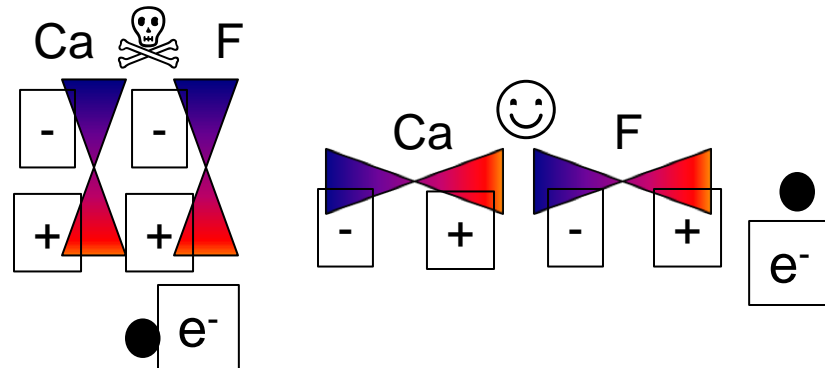Polarization always **reduces** the energy.

arbitrary electric properties

No induction by the induced dipoles.

Self-consistent to all orders of mutual induction.

Parameters are D-D polarizabilities at the two atomic centers. Parametric R-dependence of the values models exchange and overlap repulsion. This is needed for vibrational effects, VdWaals clusters, molecular mechanics.

Two forms of the two-center polarization potential, with feedback and without

- In the AJR model, Induced dipole on the metal is not allowed to polarize the anion. Silberstein's model of (1917) was extended in 1980's and 1990's by Applequist and adapted to moleclar mechanics by others (Birge, Thole) using ad-hoc short distance cutoff functions..

  1. Anisotropic effects are higher in the full model.
  2. In eiter case, this is linear system.that is easily solved for the induced dipoles and the fields.

Self-consistent polarization

$$\boldsymbol{\mu}_1 = \boldsymbol{\alpha}_1 \left(\mathbf{E}_1 + \mathbf{f}_{12,\mu} \boldsymbol{\mu}_2 \right)$$

$$\boldsymbol{\mu}_2 = \boldsymbol{\alpha}_2 \left(\mathbf{E}_2 + \mathbf{f}_{12,\mu} \boldsymbol{\mu}_1 \right)$$

Ca ☠ F

Ca ☺ F

e⁻

$$W(perp) \quad >> \quad W(para)$$
$$\text{dipole pby. } \alpha_{perp} < \quad \alpha_{para}$$

Source of anisotropy:
Induced dipoles are happier when aligned on the axis.

Induced dipole component	AJR	self-consistent
transverse (atom 1) $f_{R,\perp} = 1 - \left(\alpha_{1,\perp} \alpha_{2,\perp} / R^6 \right)$	$-\dfrac{q_t \sin \theta_1 \alpha_{1,\perp}}{r_1^2}$	$-\dfrac{q_t \sin \theta_1 \alpha_{1,\perp}}{f_{R,\perp} r_1^2} + \dfrac{q_t \sin \theta_2 \alpha_{1,\perp} \alpha_{2,\perp}}{R^3 f_{R,\perp} r_2^2}$
parallel (atom 1) $f_{R,\parallel} = 1 - \left(4 \alpha_{1,\parallel} \alpha_{2,\parallel} / R^6 \right)$	$\left(-\dfrac{q_2}{R^2} - \dfrac{q_t \cos \theta_1}{r_1^2} \right) \alpha_{1,\parallel}$	$-\left(\dfrac{q_2}{R^2} + \dfrac{q_t \cos \theta_1}{r_1^2} \right) \dfrac{\alpha_{1,\parallel}}{f_{R,\parallel}} + \dfrac{2}{R^3 f_{R,\parallel}} \left(\dfrac{q_1}{R^2} + \dfrac{q_t \cos \theta_2}{r_2^2} \right) \alpha_{1,\parallel} \alpha_{2,\parallel}$

Terms in effective multipole expansion (1-ctr)

In uniform field

$$\bar{\alpha} = \frac{\left(\alpha_{\parallel} + 2\alpha_{\perp}\right)}{3} = 2Q_0^{(\alpha)}$$

$$\Delta\alpha = \alpha_{\parallel} - \alpha_{\perp} = 3Q_2^{(\alpha)}$$

In field of point charge

$$\alpha_{\parallel,\text{uniform}} = \frac{\alpha_{1,\parallel} + \alpha_{2,\parallel} + 4\alpha_{1,\parallel}\alpha_{2,\parallel} / R^3}{1 - 4\alpha_{1,\parallel}\alpha_{2,\parallel} / R^6}$$

$$\alpha_{\perp,\text{uniform}} = \frac{\alpha_{1,\perp} + \alpha_{2,\perp}^{\text{F}} - 2\alpha_{1,\perp}\alpha_{2,\perp} / R^3}{1 - \alpha_{1,\perp}\alpha_{2,\perp} / R^6}$$

$$\alpha_{\parallel,\text{pt}} = 2\left(Q_0^{(\alpha)} + Q_2^{(\alpha)}\right) = ...$$

$$\alpha_{\perp,\text{pt}} = 2Q_0^{(\alpha)} - Q_2^{(\alpha)} = ...$$

$$\bar{\alpha}_{\text{uni}} = \frac{\left(\alpha_{\parallel} + 2\alpha_{\perp}\right)}{3} = \left(\alpha_1 + \alpha_2\right) + \frac{2\alpha_1\alpha_2\left(\alpha_1 + \alpha_2\right)}{R^6} + ...$$

$$\bar{\alpha} = \left(\alpha_1 + \alpha_2\right) + \frac{6\alpha_1\alpha_2\left(\alpha_1 + \alpha_2\right)}{R^6} + ...$$

$$\Delta\alpha_{\text{uni}} = \alpha_{\parallel} - \alpha_{\perp} = \frac{6\alpha_1\alpha_2}{R^3} + \frac{3\alpha_1\alpha_2\left(\alpha_1 + \alpha_2\right)}{R^6} + \cdots$$

$$\Delta\alpha = \alpha_{\parallel} - \alpha_{\perp} = \frac{12\alpha_1\alpha_2}{R^3} + \frac{9\alpha_1\alpha_2\left(\alpha_1 + \alpha_2\right)}{R^6} + ...$$

- Isotropic values are similar, but anisotropy is a factor of 2 greater in the point charge field than in the uniform field for the same atomic polarizabilities.
- Ab-initio that directly determines the pby from energy derivatives -- usually uniform field.
- Papers by Buckingham, Bishop and Maroulis, Kobus, and others in the Buckingham tradition studying VdW, crystals, force fields for molecule mechanics use a finite field method based on point charges, as we do.

Polarization decreases the system energy. For a Rydberg electron interacting with a cation, the cation charge **on the molecular ion** appears to increase as the electron approaches, always being larger than its bare value, giving additional attraction in the multipole series.
These effective multipole moments, determined by combining point-charge, finite-field ab-initio energies, give polarizability values.

	Effective multipole moments CaF⁺ R=3.54, CCSD(T), center of mass			
	ion core	r=30	r=20	r=15
L=0	1	1.000216806	1.000728302	1.001744283
L=1	-3.359697787	-3.358488125	-3.357120261	-3.354297508
L=2	-0.960314291	-0.872450268	-0.817670141	-0.75176334
L=3	-5.124645019	-5.008493813	-4.924469431	-4.81073013
L =4	-8.4	-7.137962566	-6.380862937	-5.464544641

test charge approaching the molecular ion →

$$W(\mathbf{r}) = \frac{1}{4\pi\varepsilon_0} \sum_L \frac{C_{L,0}(\theta,0)}{r^{L+1}} Q_L^{\text{eff}}$$

(extra r dependence hidden)

$$Q_L^{\text{eff}} \sim \left(\text{electrostatic} - \text{polarization}\right)$$

Eff. Multipole | 2-ctr no feedback | 2-ctr with feedback

$Q_L^{(S)}$	AJR	self-consistent	
$(1/r)^4$ Dipole-dipole polarizability			origin-independent
$Q_0^{(\alpha)} = \bar{\alpha}/2$	$\frac{1}{2}(\alpha_1 + \alpha_2)$	$\frac{1}{2}(\alpha_1 + \alpha_2) + \frac{3\alpha_1\alpha_2(\alpha_1 + \alpha_2)}{R^6}$ $+ \frac{8\alpha_1^2\alpha_2^2}{R^9} + \ldots$	
$Q_2^{(\alpha)} = \frac{\Delta\alpha}{3}$	$\frac{2\alpha_1\alpha_2}{R^3}$	$\frac{4\alpha_1\alpha_2}{R^3} + \frac{3\alpha_1\alpha_2(\alpha_1 + \alpha_2)}{R^6} + \ldots$	← factor of 2 from fdbk
$(1/r)^5$ Dipole-quadrupole polarizability			origin-dependent
$Q_1^{(A)}$	$2(\alpha_1 z_1 + \alpha_2 z_2) + \frac{2\alpha_1\alpha_2(z_1 + z_2)}{5R^3}$	$2(\alpha_1 z_1 + \alpha_2 z_2) + \frac{4\alpha_1\alpha_2(z_1 + z_2)}{5R^3} + \ldots$	
$Q_3^{(A)}$	$\frac{18\alpha_1\alpha_2(z_1 + z_2)}{5R^3}$	$\frac{36\alpha_1\alpha_2(z_1 + z_2)}{5R^3} + \ldots$	← factor of 2 from fdbk
$(1/r)^3$ Quadrupole invariant (COC): $^{(1)}\tilde{Q}_2 = Q_2 - (Q_1^2/Q_0)$			origin-independent
$Q_2^{(0)}Q_0^{(0)} - Q_1^{(0)2}$ $= \Theta_{zz}^{(0)}q_t^{(0)} - \mu_z^{(0)2}$	$R^2 Z_1 Z_2 + \frac{2Z_2^2\alpha_1 + 2Z_1^2\alpha_2}{R} -$ $\frac{Z_2^2\alpha_1^2 + 6Z_1 Z_2\alpha_1\alpha_2 + Z_1^2\alpha_2^2}{R^4} + \ldots$	$R^2 Z_1 Z_2 + \frac{2Z_2^2\alpha_1 + 2Z_1^2\alpha_2}{R} -$ $\frac{Z_2^2\alpha_1^2 + 14Z_1 Z_2\alpha_1\alpha_2 + Z_1^2\alpha_2^2}{R^4} + \ldots$	

These are power series in 1/R, not very convergent, but easier to interpret than exact forms.

Change of origin for linear molecule moments

$$Q_L(z-a) = \sum_{j=0}^{L} (-a)^{L-j} \binom{L}{j} Q_j(z)$$

For an ion, the dipole moment and higher depend on origin, but there are combinations that are origin-independent.

$$^{(0)}\tilde{Q}_L = \underbrace{\sum_{j=0}^{L} \binom{L}{j}\left(\frac{-Q_1}{Q_0}\right)^j Q_{L-j}}_{\text{evaluate using any origin}}$$

$$^{(1)}\tilde{Q}_L = \sum_{j=0}^{L} \left(\pm\sqrt{-^{(1)}\tilde{Q}_2}\right)^j \binom{L}{j} {}^{(1)}\tilde{Q}_{L-j}$$

*Family of invariants with dipole = 0 (ctr of charge moments)*

Invariants with Q_2 (quadrupole) = 0 (ctr of dipole invariants)

These special points are potential expansion origins, because they zero one contribution to the energy, defining a good stopping point in the expansion.
In addition, a **center of dipole polarizability** can be defined that optimizes the expansion through (octopole + dipole polarizability) $1/r^4$ terms.

How large an orbital angular momentum is required for it to be treaded as non-penenetrating with a particular effective potential?

* Accuracy of an effective potential depends on the origin used to expand it.
* For a rotating diatomic, COM should be used. (JKGW, Ch. J.)
* Omission of the inconvenient dipolar term in the effective potential implies the use of the poorly-convergent COC origin.
* JKGW suggests a perturbation-theory adjustment of some matrix elements (dipole-drag), but this is less valid for extremely large dipole moments, and especially for low Lambda states.
* The result is uncertainty in the best way to determin core properties from Rydberg spectr.
* Solutions:
- Zon group reduced / added MQDT
- Altunata, Coy, RWF dipole reduction MQDT
- Non-perturbative effective potential treatment including dipole mixing explicitly
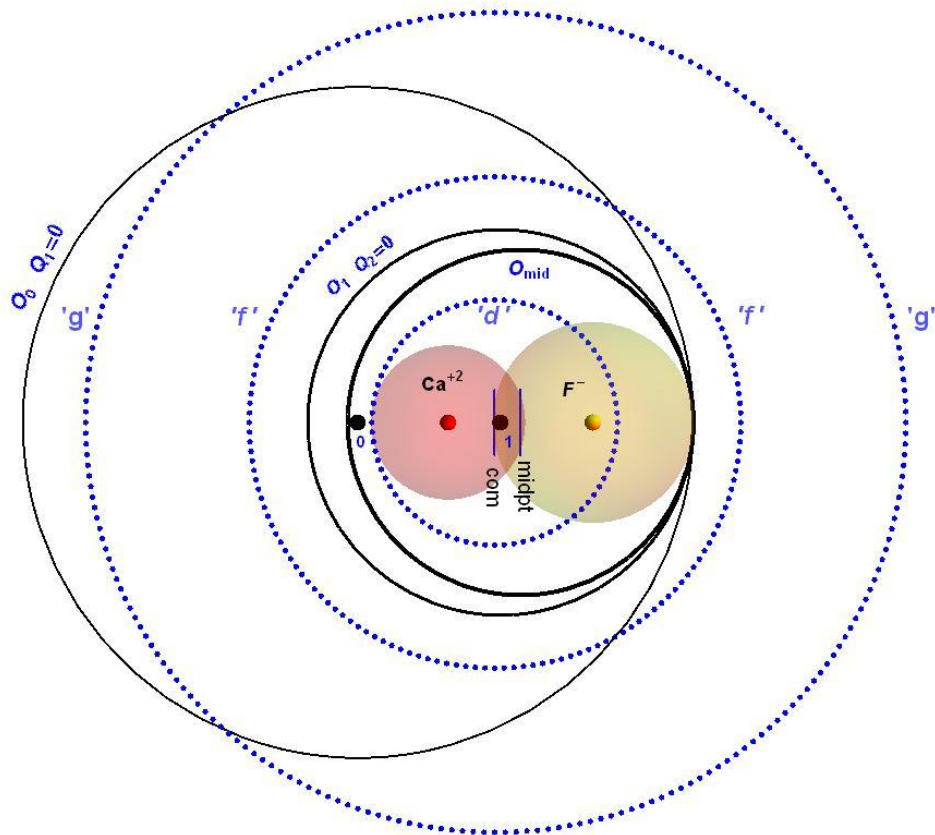
Dotted lines are closest approach of orbital angular momentum states (COM-based).
Solid circles are inner limit of convergence of the multipole series (origins COC, CODip, midpoint)

At long range, the electron sees the center of charge. On approach, it is surprised by the displaced cation attraction, and by anionic repulsion. Complexity is the result: mixing of orbital angular momentum,stroboscopic Kepler-rotation resonances, and , shape-resonance coupling to dissociating states.

Summary

- Single-center multipole expansions allow for arbitrary electric properties in the core
- Two-center potentials are contrained by the limited parametrization, and my not be able to match ab-initio values.
- Single-center multipole expansion is poorly convergent when the origin is chosen outside the charge distribution, especially when the center of charge is used for polar molecules. The Watson drag correction may be inadequate for large dipole moments.
- Two forms of the two-center are in the literature, AJR with limited mutual induction, and the expression with self-consistent mutual induction. Difference in the two potentials include
  - Both potentials may be adjusted to match **exactly** the static dipole and the quadrupole moments of the molecular ion.
  - In the properties of the molecular ion, the full potential predictes a larger value of the DD pby anisotropy.
  - For the inferred atomic polarizabilities, the values and dependence on internuclear separation are different, smaller values neded for the full potential.

Feedback Effect on Quadrupole Invariant, $^{(0)}Q_2 = \Theta - \mu^2/e$
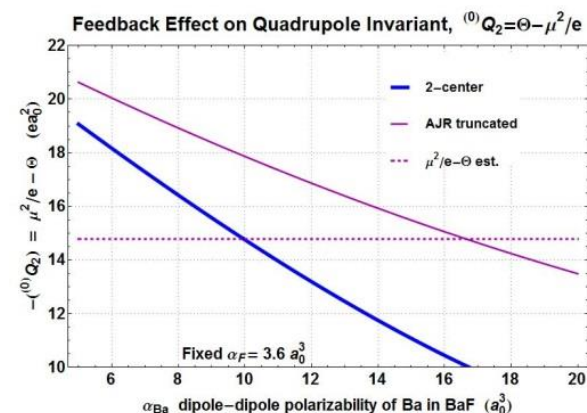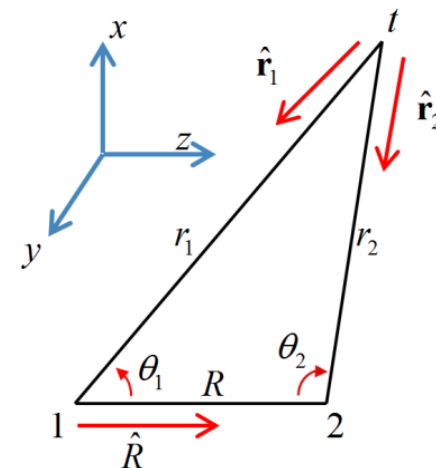
Effect of Ion Core Dipole Polarizability

This example is schematic, based on a 'f' complex group that may be described using (Lambda, Kronig symmetry, $(\Sigma,+)$ at top) or L_R (N-N$^+$, -3 to +3, top to bottom).
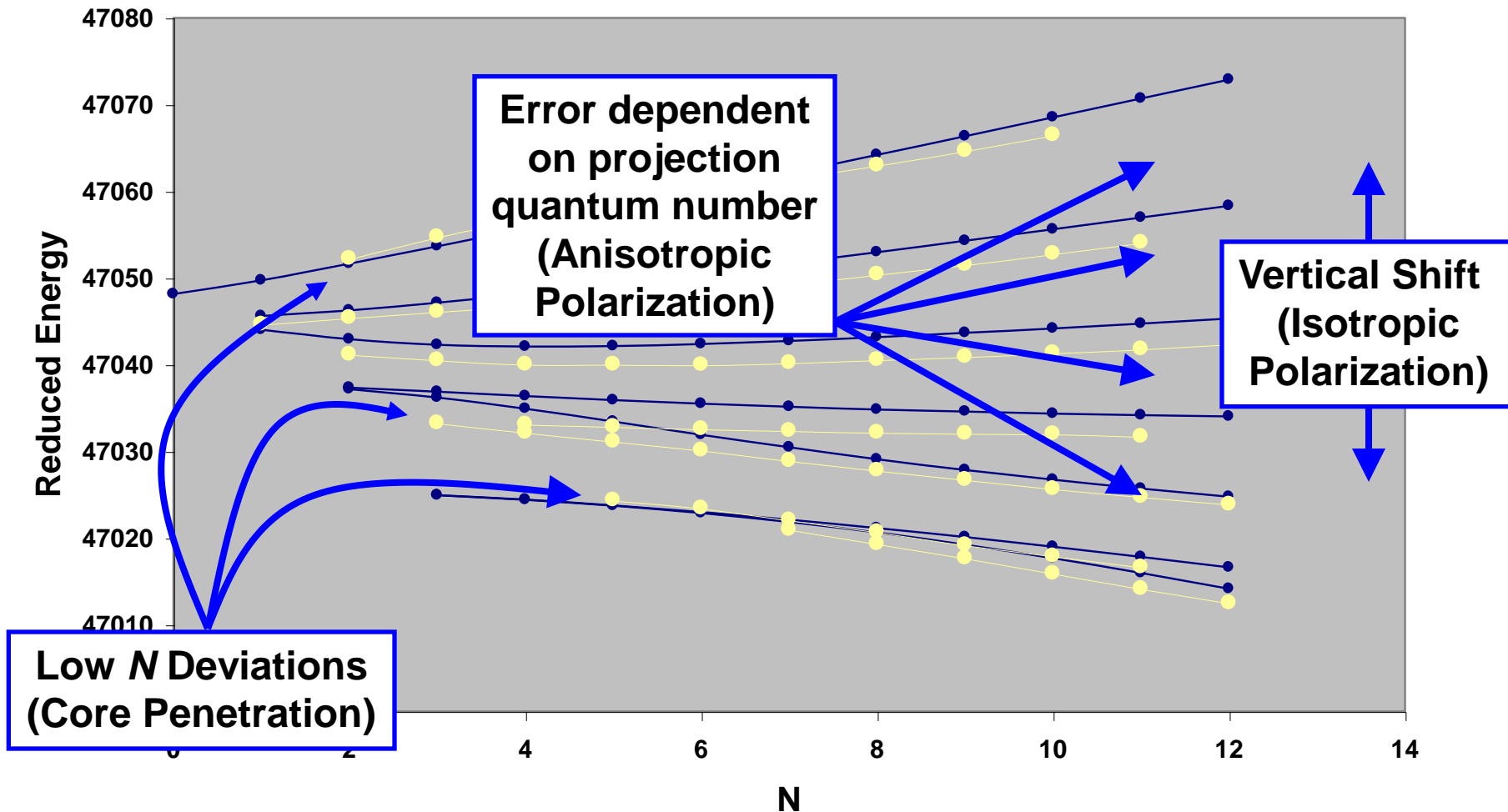
Effect of Origin and Feedback on Ion Core Properties

BaF potential (R_{eq}=3.93 a_0)						
Potential	Points	AJR	Full 2-center			
Origin	COM		COM	COα ($\vec{O}_\alpha$)	COD ($\vec{O}_1$)	COC($\vec{O}_0$)
$z-z_{Ba}$ (a_0)	0.476		0.476	1.077	1.664	-2..65
α(Ba,F)	(0,0)	(11.4, 4.7)	← matches expt.→	(10.0,3.6)		
$^{(0)}Q_2$, r^{-3} $(Q_2 - Q_1^2/Q_0)$	-30.9	-14.78	taken from expt. -14.76			
$\Delta\alpha/\bar{\alpha}$	NA	0.33	** 0.61 ** large anisotropy			
$(Q_0^{(\alpha)}, Q_2^{(\alpha)}), r^{-4}$	(0,0)	(8.05, 1.76)	(7.26,2.95)			
$(Q_1^{(A)}, Q_3^{(A)}), r^{-5}$	(0,0)	(22.7, 9.5)	(18.2, 14.4)	(0, 8.0)	(-17.7, 1.8)	(98.5, 43.6)
$Q_1^{(0)}, r^{-2}$	-4.41	-2.72	-2.65	-3.25	-3.84	0
$Q_2^{(0)}, r^{-3}$	-11.48	-7.40	-7.72	-4.16	0	-14.76
$Q_3^{(0)}, r^{-4}$	-41.45	-14.9	-15.97	-5.15	-1.39	-114.8
$Q_4^{(0)}, r^{-5}$	-142.3	-23.5	-28.8	-4.68	1.56	-673.1

Zero-field

atomic units

pure ionic inadequate.

center of mass
Core zero-field
electrostatics are the
same. Pby differ.

ctr of dipole polarizability

ctr of dipole

COC not convergent

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End post-summary extra slides