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Electric potential invariants and ions-in-molecules effective potentials for molecular Rydberg states

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The dependence of multipole moments and polarizabilities on external fields appears in many applications including biomolecular molecular mechanics, optical non-linearity, nanomaterial calculations, and the perturbation of spectroscopic signatures in atomic clocks. Over a wide range of distances, distributed multipole and polarizability potentials can be applied to obtain the variation of atom-centered atoms-in-molecules electric properties like bonding-quenched polarizability. For cylindrically symmetric charge distributions, we examine single-center and atom-centered effective polarization potentials in a non-relativistic approximation for Rydberg states. For ions, the multipole expansion is strongly origin-dependent, but we note that origin-independent invariants can be defined. The several families of invariants correspond to optimized representations differing by origin and number of terms. Among them, a representation at the center of dipole polarizability optimizes the accuracy of the potential with terms through $1/r^4$. We formulate the single-center expansion in terms of polarization-modified effective multipole moments, defining a form related to the source-multipole expansion of Brink and Satchler. Atom-centered potentials are an origin independent alternative but are limited both by the properties allowed at each center and by the neglected effects like bond polarizability and charge flow. To enable comparisons between single-center effective potentials in Cartesian or spherical form and two-center effective potentials with differing levels of mutual induction between atomic centers, we give analytical expressions for the bond-length and origin-dependence of multipole and polarizability terms projected in the multipole and polarizability expansion of Buckingham. The atom-centered potentials can then be used with experimental data and *ab initio* calculations to estimate atoms-in-molecules properties. Some results are given for BaF^+ and HF showing the utility and limitations of the approach. More detailed results on $\text{X}^1\Sigma^+ \text{CaF}^+$ are published separately. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4968228>]

INTRODUCTION

The electric polarizability of atoms and molecules is a key element in the prediction of atomic and molecular properties, including molecular dynamics and solvent shifts,^{1,2} optical non-linearity, the stability of atomic clock transitions, and static and dynamic properties of nanomaterials, molecules, clusters, and ions.^{3–6} Dynamic polarization has also been shown to be important in biomolecular molecular mechanics although there remain variations in the accuracy with which polarization is treated.^{7–10}

Rydberg spectroscopy is recognized as a sensitive probe of electric properties of the ion core, and its reach is now being extended by the development of microwave techniques with 1000-fold higher resolution than standard laser methods.¹¹ Molecules that can be viewed as effective one-electron systems and systems which can be treated by the atoms-in-molecules multi-center approximation are especially useful in developing extended theoretical methods, interpreting new experimental techniques, and providing a fundamental understanding of few-body quantum systems.

In this paper, we start from a distributed-polarizability two-center effective potential for polar molecules known as

the Applequist-Silberstein¹² or dipole-induced-dipole (DID) model and make connections to *ab initio* calculations and single-center multipolar perturbation theory. The single-center multipole and polarizability expansion, pioneered by Buckingham,¹³ is a convenient meeting place between approaches that include *ab initio* calculations, multi-center effective potentials, multi-channel quantum defect theory (MQDT) calculations using an effective potential,^{14–17} and quantum defects fitted to experimental data.^{18,19} This combination of approaches extends previous work by making a connection between atomic and molecular properties, by comparing predictions of effective potentials using different models of mutual polarization between atomic centers, and by making it possible to use a phenomenological effective potential to predict multipole moments and polarizabilities.

The development of potentials for the interaction of an atomic or molecular ion with fields or charge distributions has been approached from different perspectives. Non-penetrating Rydberg states are approximately atomic even for molecular ion cores, although the single-center form is known to introduce some inaccuracy.²⁰ Potential forms for isolated atomic ions have been derived and discussed in works such as those by Clark, Greene, and Miecznik²¹ and by Woods and

Lundeen.²² Additional relativistic terms have been derived by a number of authors.^{23–25} The reference point for very high accuracy analysis to atoms has been the work by Drachman^{26–28} which has led to impressive results including relativistic and QED effects.^{29,30} Limiting behavior in the Rydberg inverse Born-Oppenheimer region has been considered by Zon's group in several publications, including Elfimov *et al.*³¹ for the long-range dipole potential of polar molecules, and Dorofeev *et al.*,³² but these treatments omit the full complexity of interactions with a rotating core.³³ Frequency dependent polarizability is important at frequencies approaching electronic transitions.^{34–36}

Because there are no retardation effects when the point charge is moving much slower than the core electrons, we provisionally omit those terms and focus on approximations for electric properties of molecular ions which are ionic in character and amenable to an atoms-in-molecule approach. This work develops effective potentials that can yield transferable atomic properties including polarizability quenching by Pauli repulsion and charge overlap.

The phenomenological approach used here can be coordinated with single-center or multi-center effective potentials and with calculations by *ab initio* methods. Our approach follows from the work on polarization and intra- and inter-molecular forces of Buckingham,^{13,37} Stone,^{38–40} Maroulis,^{41–44} Schmidt,⁵ and others.^{45,46} Multi-center distributed multipole and polarizability potentials have been extensively studied, with expansion centers sited at atom and/or bond positions⁴⁷ or more generally located,⁴⁰ and have been found to improve accuracy and convergence of potentials in applications including van der Waals clusters.⁴⁸ Polarization effects are also important in molecular mechanics simulations, where generic but chemically specific atomic polarizabilities^{49,50} have been used, but there is a trend toward more rigorous approaches to solvent/cluster and surface interactions, such as that by the groups of Gordon² and Wodtke.⁵¹ Polarizability and its dependence on internuclear separation are important in ionic Rydberg systems with vibrational and rotational excitation due to its effect on spectroscopy and dynamics, including autoionization and predissociation.^{52–55}

Our focus is on the information on core electronic structure that can be obtained from high-resolution Rydberg spectra of diatomic and larger molecules and on forms of polarization potentials for more general applications. We make use of *ab initio* calculations, distributed polarizability models, and the symmetry-reduced general perturbation theory expansion to develop a framework for the interpretation of non-penetrating molecular Rydberg states. Especially for polar molecules, we will show that the treatment of states by long-range models as non-penetrating depends not only on the orbital angular momentum but also on the form and coordinate origin of the potential used for the analysis.

EXPANSION OF THE POTENTIAL IN CARTESIAN AND SPHERICAL COORDINATES

In the multipole expansion, the energy of a polarizable charge distribution in a general external potential is written as a single-center expansion using the Einstein summation

convention on repeated subscripts as

$$W = Q_0 \mathcal{V} + \mu_\alpha \mathcal{V}_\alpha + \frac{1}{3} \Theta_{\alpha\beta} \mathcal{V}_{\alpha\beta} + \frac{1}{15} \Omega_{\alpha\beta\gamma} \mathcal{V}_{\alpha\beta\gamma} + \dots$$

$$= \sum_{L=0}^{\infty} \frac{1}{(2L-1)!!} \xi_{\alpha\beta\dots\gamma} \mathcal{V}_{\alpha\beta\dots\gamma}, \quad (1)$$

where the terms are in Cartesian coordinates, and Cartesian axes and derivatives indicated by lower case Greek subscripts,⁴⁰ and the number of subscripts is L , including $L=0$, which is the Coulomb potential term. \mathcal{V} is the arbitrary external potential whose value and spatial derivatives are evaluated at the expansion center. The potential \mathcal{V} may have arisen from a crystal field, other parts of the molecule, or from a Rydberg electron.

The monopole, dipole, quadrupole, octupole, and higher moments (Q_0 , μ_α , $\Theta_{\alpha\beta}$, $\Omega_{\alpha\beta\gamma}$, ...) and the generic multipole $\xi_{\alpha\beta\dots\gamma}$ are polarization-modified effective moments. As explained in the work of Stone,⁴⁰ this form of the interaction energy has made use of the Poisson equation to define multipole moments which are traceless over repeated subscripts and are unchanged by permutation of the subscripts. They can be evaluated by a sum over the charge distribution^{40,56} that involves the Coulomb field magnitude $V(\vec{\mathbf{a}})$ and coordinate derivatives $V_{\alpha\beta\dots\gamma}(\vec{\mathbf{a}})$ from each element of charge in the ion core,

$$\xi_{\alpha\beta\dots\gamma} = \frac{1}{L!} \sum_{\text{all } \vec{\mathbf{a}}} q_{\vec{\mathbf{a}}} a^L (-1)^L \left[a^{L+1} V_{\alpha\beta\dots\gamma}(\vec{\mathbf{a}}) \right],$$

$$a = |\vec{\mathbf{a}}|, (-1)^L V_{\alpha\beta\dots\gamma}(\vec{\mathbf{a}}) = \left(-\frac{\partial}{\partial a_\alpha} \right) \dots \left(-\frac{\partial}{\partial a_\gamma} \right) \left(\frac{1}{a} \right). \quad (2)$$

The parameter $\vec{\mathbf{a}}$ is the vector from the expansion origin to the charge element at $\vec{\mathbf{a}}$ with charge $q_{\vec{\mathbf{a}}}$. These equations distinguish between the environmental potential, field, and field gradients $\mathcal{V}_{\alpha\beta\dots\gamma}$ that might be applied to the charge distribution, and the Coulomb potential from each element of the charge distribution, written as $V_{\alpha\beta\dots\gamma}(\vec{\mathbf{r}})$, which determines multipoles of the distribution. Because the bracketed term in the first line is a function of angles only, high- L moments are dominated by charges distant from expansion center, so that the higher multipole moments will diverge rapidly if the origin is poorly chosen. For a continuous charge distribution, a Cartesian multipole operator, $\hat{\xi}_{\alpha\beta\dots\gamma}(\vec{\mathbf{r}})$, can be integrated over the charge density to determine the Cartesian multipole moments,

$$\xi_{\alpha\beta\dots\gamma} = \int d^3\vec{\mathbf{r}} \rho(\vec{\mathbf{r}}) \hat{\xi}_{\alpha\beta\dots\gamma}(\vec{\mathbf{r}}), \text{ where}$$

$$\hat{\xi}_{\alpha\beta\dots\gamma}(\vec{\mathbf{r}}) = \frac{1}{L!} r^{2L+1} (-1)^L V_{\alpha\beta\dots\gamma}(\vec{\mathbf{r}}). \quad (3)$$

In perturbation theory, the energy of the molecular ion modified by the external potential is a sum of terms: the energy of the static charge distribution without polarization ($W^{(0)}$), the energy due to a linear polarization response ($W^{(2)}$, polarizability), and higher-order polarization ($W^{(HP)}$, hyperpolarizability). The interaction energy with an external potential is given by the following equations, again using the Einstein summation convention on repeated subscripts:

$$W(\mathbf{r}) = W^{(0)} + W^{(2)} + W^{(HP)}, \quad (4)$$

$$\begin{aligned}
W^{(0)} &= \sum_{L=0}^{\infty} \frac{1}{(2L-1)!!} \xi_{\alpha\beta\cdots\gamma}^{(0)} \mathcal{V}_{\alpha\beta\cdots\gamma} \\
&= Q_0 \mathcal{V} + \mu_{\alpha}^{(0)} \mathcal{V}_{\alpha} + \frac{1}{3} \Theta_{\alpha\beta}^{(0)} \mathcal{V}_{\alpha\beta} + \frac{1}{3 \cdot 5} \Omega_{\alpha\beta\gamma}^{(0)} \\
&\quad \times \mathcal{V}_{\alpha\beta\gamma} + \frac{1}{3 \cdot 5 \cdot 7} \Phi_{\alpha\beta\gamma\delta}^{(0)} \mathcal{V}_{\alpha\beta\gamma\delta} + \cdots, \quad (5)
\end{aligned}$$

$$\begin{aligned}
W^{(2)} &= -\frac{1}{2} \alpha_{\alpha\beta} \mathcal{V}_{\alpha} \mathcal{V}_{\beta} - \frac{1}{3} A_{\alpha,\beta\gamma} \mathcal{V}_{\alpha} \mathcal{V}_{\beta\gamma} - \frac{1}{6} C_{\alpha\beta,\gamma\delta} \mathcal{V}_{\alpha\beta} \mathcal{V}_{\gamma\delta} \\
&\quad - \frac{1}{15} E_{\alpha,\beta\gamma\delta} \mathcal{V}_{\alpha} \mathcal{V}_{\beta\gamma\delta} - \cdots, \quad (6)
\end{aligned}$$

$$\begin{aligned}
W^{(HP)} &= +\frac{1}{6} \beta_{\alpha\beta\gamma} \mathcal{V}_{\alpha} \mathcal{V}_{\beta} \mathcal{V}_{\gamma} + \frac{1}{6} B_{\alpha,\beta,\gamma\delta} \mathcal{V}_{\alpha} \mathcal{V}_{\beta} \mathcal{V}_{\gamma\delta} \\
&\quad - \frac{1}{24} \gamma_{\alpha\beta\gamma\delta} \mathcal{V}_{\alpha} \mathcal{V}_{\beta} \mathcal{V}_{\gamma} \mathcal{V}_{\delta} + \cdots. \quad (7)
\end{aligned}$$

The superscript (0) on the multipole moments indicates a static moment of the unperturbed ion core. The notation $(\alpha_{\alpha\beta}, A_{\alpha,\beta\gamma}, C_{\alpha\beta,\gamma\delta}, E_{\alpha,\beta\gamma\delta}, \beta_{\alpha\beta\gamma}, \gamma_{\alpha\beta\gamma\delta}, B_{\alpha,\beta,\gamma\delta})$ for the various polarizability and hyperpolarizability coefficients is the conventional labels used by Buckingham,^{13,57} Stone,⁴⁰ Maroulis,^{44,58} and others.⁵⁹ We have followed Anthony Stone in using external potential terms $\mathcal{V}_{\alpha\beta\cdots\gamma}$ instead of the field notation $F_{\alpha\beta\cdots\gamma}$ since it is a bit more convenient for charged systems. This introduces a sign change for each \mathcal{V} , because

$$F_{\alpha\beta\cdots\gamma} = -(\nabla_{\alpha} \cdots \nabla_{\gamma}) \mathcal{V} = -\mathcal{V}_{\alpha\beta\cdots\gamma}. \quad (8)$$

When field F is used in the expansion, the conventional sign of each induction term is negative, which is motivated by the property that polarization reduces the energy. When the potential is used in the expansion, terms with an odd number of potential factors have a positive sign.

To specialize to the interaction with a slowly moving Rydberg electron, the potential V is taken to be the Coulomb potential from a test charge. At the origin chosen for the multipole expansion, the potential factors from a charge q_t at position $\vec{\mathbf{r}}$ are given by the following:

$$\begin{aligned}
\mathcal{V}_{\alpha\beta\cdots\gamma} &\rightarrow V_{\alpha\beta\cdots\gamma}(\vec{\mathbf{r}}, q_t) = q_t (-1)^L V_{\alpha\beta\cdots\gamma}(\vec{\mathbf{r}}) \\
&= q_t \left(-\frac{\partial}{\partial \alpha} \right) \cdots \left(-\frac{\partial}{\partial \gamma} \right) \left(\frac{1}{r} \right), \quad (9)
\end{aligned}$$

where small Greek letters are from the set of Cartesian coordinates (x, y, z), and r is the radial distance. The radial and angular dependence of the point charge potential factors $\mathcal{V}_{\alpha\beta\cdots\gamma}$ determines the dependence of the energy on the test-charge distance and polar angle. Some polarization-modified Cartesian multipole moments in general form are shown here,^{13,60,61}

$$\begin{aligned}
\mu_{\alpha} &= \frac{\partial W}{\partial \mathcal{V}_{\alpha}} = \mu_{\alpha}^{(0)} - \alpha_{\alpha\beta} \mathcal{V}_{\beta} - \frac{1}{3} A_{\alpha,\beta\gamma} \mathcal{V}_{\beta\gamma} - \frac{1}{15} E_{\alpha,\beta\gamma\delta} \mathcal{V}_{\beta\gamma\delta} \\
&\quad + \frac{1}{2} \beta_{\alpha\beta\gamma} \mathcal{V}_{\beta} \mathcal{V}_{\gamma} + \frac{1}{3} B_{\alpha,\beta,\gamma\delta} \mathcal{V}_{\beta} \mathcal{V}_{\gamma\delta} \\
&\quad - \frac{1}{6} \gamma_{\alpha\beta\gamma\delta} \mathcal{V}_{\beta} \mathcal{V}_{\gamma} \mathcal{V}_{\delta} + \cdots, \quad (10)
\end{aligned}$$

$$\begin{aligned}
\Theta_{\alpha\beta} &= 3 \frac{\partial W}{\partial \mathcal{V}_{\alpha\beta}} = \Theta_{\alpha\beta}^{(0)} - A_{\gamma,\alpha\beta} \mathcal{V}_{\gamma} - C_{\alpha\beta,\gamma\delta} \mathcal{V}_{\gamma\delta} \\
&\quad + \frac{1}{2} B_{\gamma,\delta,\alpha\beta} \mathcal{V}_{\gamma} \mathcal{V}_{\delta} + \cdots, \quad (11)
\end{aligned}$$

$$\Omega_{\alpha\beta\gamma} = 15 \frac{\partial W}{\partial \mathcal{V}_{\alpha\beta\gamma}} = \Omega_{\alpha\beta\gamma}^{(0)} - E_{\gamma,\alpha\beta\gamma} \mathcal{V}_{\gamma} \cdots. \quad (12)$$

Symmetry operations in the point group of the molecular ion will leave the energy unchanged, leading to a reduction in the number of independent parameters. Applequist⁶² has shown that the equations like (10)–(12), which were given for the general case by Buckingham, can also be applied after symmetry-reduction of the energy expression. To maintain the symmetry of the energy expression in a perturbed environment, the perturbation must also have the molecular symmetry, or be sufficiently weak, or the Born-Oppenheimer approximation must apply due to the difference between the Rydberg and core time scales.

A general scalar field can be expanded in spherical harmonics with coefficients dependent on the radial coordinate. The $1/r^{(l+1)}$ r -dependence of static multipole terms is a special property of the Coulomb potential. For a general scalar field, $f(r, \Omega)$ (such as interaction energy including polarizability), the coefficients can have a more general radial dependence. Non-Coulomb terms in the interaction energy between two charge distributions include induction and dispersion terms as well as exchange interactions. Only induction energy will be considered here since dispersion energy is zero for the interaction between a Rydberg electron and the ion core. We also omit the exchange interactions between the Rydberg electron and the ion core.

In the spherical-tensor multipole expansion corresponding to the Cartesian form, the interaction energy $W(\mathbf{r})$ is written in terms of polarization-modified effective spherical multipole moments, $Q_{L,M}(r, q_{\text{test}})$, which are a function of test charge radial distance,

$$(4\pi\epsilon_0) W(\vec{\mathbf{r}}, q_t) = \sum_{L,M} q_t Q_{L,M}(r, q_t) \frac{C_{L,M}^*(\theta, \varphi)}{r^{L+1}}. \quad (13)$$

The factor $4\pi\epsilon_0$ is of unit magnitude in atomic units, but not dimensionless (units $e^2/a_0 E_h$),⁶³ and $C_{L,M}$ are renormalized spherical harmonics.⁶⁴ The spherical multipole operator is $\hat{Q}_{L,M}(\vec{\mathbf{r}})$, analogous to Equation (2),

$$\begin{aligned}
\hat{Q}_{L,M}(\vec{\mathbf{r}}) &= r^L C_{L,M}^*(\theta, \phi), \\
Q_{L,M} &= \int d^3\vec{\mathbf{r}} \rho(\vec{\mathbf{r}}) \hat{Q}_{L,M}(\vec{\mathbf{r}}). \quad (14)
\end{aligned}$$

The effective moments, as modified by polarization, can be obtained by projecting the perturbed energy on a sphere at a fixed distance, r , onto the multipole operator,

$$\begin{aligned}
q_t Q_{L,M}(r, q_{\text{test}}) &= \left(\frac{2L+1}{4\pi} \right) r^{L+1} \int_0^\pi d\theta \sin\theta \int_0^{2\pi} d\varphi \\
&\quad \times C_{L,M}(\theta, \varphi) (4\pi\epsilon_0) W(r, \theta, \varphi). \quad (15)
\end{aligned}$$

The Hamiltonian for linear molecules is usually assumed to possess full cylindrical symmetry so that only $M = 0$ moments are non-zero. This $M = 0$ simplification does not apply when the core is in a $\Lambda > 0$ electronic state, as recently reviewed and clarified by Bruna and Grein.⁶⁵ The largest $\Lambda > 0$ asymmetries leading to M -dependence appear in quadrupole moments and dipole-dipole polarizabilities of Π states, with anisotropies of higher Λ states being small. Examples of

anisotropy effects include spin-selective collisional dissociation of water to OH ($X^2\Pi$) Λ doublets (Table 1 in the work of Gwinn *et al.*⁶⁶). The point polarizable model requires atoms-in-molecules localization in the electronic structure and can only be applied for a limited range of bond lengths for hydrides. This is discussed further in the section on hydrogen fluoride. Considering a more ionic case (and following a reviewer's suggestion), we performed *ab initio* calculations on $X^2\Pi$ CaO⁺ with the result that the parallel polarizability α_{zz} is approximately twice the perpendicular α_{xx} and α_{yy} , and the difference ($\alpha_{yy} - \alpha_{xx}$) is about 10% of the parallel value. Quadrupole moment anisotropies are a more complex issue because of the usual reduction to traceless form of the quadrupole tensor and the strong dependence of the quadrupole on origin location for a polar ion. Full cylindrical symmetry applies to Rydberg states with a Σ ion core or to Σ linear polyatomics. Limiting to full cylindrical symmetry, we drop the M subscript and write the energy including all polarization terms as

$$W(\mathbf{r}) = \sum_L W_L(\mathbf{r}), \text{ where} \quad (16)$$

$$W_L(\mathbf{r}) = \frac{1}{4\pi\epsilon_0} q_t Q_L(r, q_t) \frac{C_{L,0}(\theta, \varphi)}{r^{L+1}}.$$

$Q_L(r, q_t)$ is an effective moment that combines all terms with a particular angular dependence and includes all polarizability terms that contribute to that angular dependence with a modified radial dependence,

$$q_t Q_L(r, q_t) = q_t Q_L^{(0)} - \sum_{S, L \text{ with } Q_L^{(S)} \neq 0} (-1)^{n_S} q_t^{n_S} \frac{Q_L^{(S)}}{r^{k_{S,L}}}. \quad (17)$$

The effective moments are a useful construct because *ab initio* calculations can be used to decouple the contribution of different polarizability types by projecting out terms that differ by angular and radial dependence. This method of including polarizability terms with their additional radial dependences is essentially identical to the Brink and Satchler source-multipole expansion for an arbitrary scalar distribution⁶⁴ (Section 4.10.5, pp. 4.55-4.56). We mark the terms by polarization type S , instead of using just the power $k_{S,L}$: $Q_L^{(S)} \Leftrightarrow Q_{L,0}^{(S)}$, $n = k_{S,L}$ (B & S), since multiple polarizability types may contribute to the same radial dependence.

The energy terms are either static core multipole energies $W^{(0)}(\mathbf{r})$ or energies from core polarization $W^{(S)}(\mathbf{r})$, as follows:

$$W(\mathbf{r}) = \sum_{S \in \{0, \alpha, \beta, \gamma, \delta, A, B, C, E, \dots\}} W^{(S)}(\mathbf{r}),$$

$$W^{(0)}(\mathbf{r}) = \frac{q_t}{4\pi\epsilon_0} \sum_L Q_L^{(0)} \frac{C_{L,0}(\theta, 0)}{r^{L+1}}, \quad (18)$$

$$W^{(S)}(\mathbf{r}) = - \frac{(-1)^{n_S} q_t^{n_S}}{4\pi\epsilon_0} \sum_{\{L_S\}} \frac{C_{L_S,0}(\theta, 0)}{r^{L_S+1}} \frac{Q_{L_S}^{(S)}}{r^{k_{S,L_S}}}.$$

The (0)-superscripted multipoles $Q_L^{(0)}$ in (17) are the multipole moments of the ion core, determined in the absence of an external potential or test charge. The energy with angular dependence L is expressed in terms of $Q_L^{(0)}$ and $Q_L^{(S)}$, separating static multipoles from polarization. The overall sign of the sum of polarizability terms is negative by convention, making the most polarizability coefficients positive, since polarization reduces the energy. The label S enumerates polarization terms, a particular one of which contributes with angular dependences $\{L_S\}$. The value n_S is the number of potential factors (V) in the energy term of type (S), which has a number of coordinate derivatives n_{der} . k_{S,L_S} is the difference between the radial dependence of (S)-polarizability energy ($n_S + n_{\text{der}}$) and $L_S + 1$. For example, for the dipole-dipole polarizability, $S = \alpha$, $W^{(\alpha)} = -\alpha_{\alpha\beta} V_\alpha V_\beta / 2$, so n_α is 2, n_{der} is 2, and $W^{(\alpha)} \propto r^{-4}$. Symmetry leads to the contributions from $L = 0$ and 2, namely, $Q_0^{(\alpha)}$, with $k_{\alpha,0} = (n_S + n_{\text{der}}) - (L + 1) = 4 - 1 = 3$, and $Q_2^{(\alpha)}$, with $k_{\alpha,2} = 1$. For all static multipoles, $Q_L^{(0)}$, $n_{(0)}$ is 1, and $k_{(0),L} = 0$.

The angular and radial dependences of terms appearing in the spherical expansion are identified in Table I. The number of independent parameters for a cylindrically symmetric in the Cartesian expansion is given in Appendix A, Table VI. The polarizability parameters $\alpha, \beta, \gamma, \delta, A, B, C, E, \dots$ are the properties of the core charge distribution and have no dependence on the state of the Rydberg electron. The energy of a particular Rydberg electronic state is determined by the diagonalization of the potential in a Rydberg basis. The static dipole of the ion core produces ℓ -mixing and intensity anomalies⁶⁷ and

TABLE I. Contributions to the energy of a cylindrically symmetric charge distribution interacting with a point-charge by effective multipole moment types dipole-dipole (α), dipole-quadrupole (A), quadrupole-quadrupole (C), dipole-octupole (E), dipole hyperpolarizabilities ($\beta(DDD)$, $\gamma(DDDD)$, $B(DDQ)$), quadrupole-octupole (Q,O), and octupole-octupole (O,O). Terms with identical angular and radial dependence cannot be distinguished.

$W_L^{(S)} \sim \frac{q_t Q_L^{(S)}}{r^{k_{S,L}}} \frac{C_{L,0}}{r^{L+1}}$	Effective moment terms (cylindrical symmetry)							
$(\frac{1}{r})^{k_{S,L}}$	1	$\frac{1}{r}$	$\frac{1}{r^2}$	$\frac{1}{r^3}$	$\frac{1}{r^4}$	$\frac{1}{r^5}$	$\frac{1}{r^6}$	$\frac{1}{r^7}$
$L = 0$	$Q_0^{(0)}$	0	0	$Q_0^{(\alpha)}$	0	$Q_0^{(C)}$	$Q_0^{(B)}$	$Q_0^{(\gamma)} + Q_0^{(O,O)}$
$L = 1$	$Q_1^{(0)}$	0	0	$Q_1^{(A)}$	$Q_1^{(\beta)}$	$Q_1^{(Q,O)}$
$L = 2$	$Q_2^{(0)}$	$Q_2^{(\alpha)}$	0	$Q_2^{(C)} + Q_2^{(E)}$	$Q_2^{(B)}$	$Q_2^{(\gamma)} + Q_2^{(O,O)}$
$L = 3$	$Q_3^{(0)}$	$Q_3^{(A)}$	$Q_3^{(\beta)}$	$Q_3^{(Q,O)}$
$L = 4$	$Q_4^{(0)}$	$Q_4^{(C)} + Q_4^{(E)}$	$Q_4^{(B)}$	$Q_4^{(\gamma)} + Q_4^{(O,O)}$

contributes to the energy in first order if the quantum-defect-labeled Zon⁶⁸/Watson⁶⁹ Coulomb-dipole basis is used,⁶⁷ but is off-diagonal in the usual Coulomb (hydrogenic) basis.

Applications to Rydberg molecules are essentially the same as the polarization effective-potential model described by Watson,⁷⁰ whose treatment builds on earlier Refs. 71–73. The non-adiabatic long-range ($1/r^5$) correction of Dalgarno *et al.*⁷⁴ (also Spruch and Kelsey^{25,75,76}) for a moving electron around an arbitrary molecular ion is not included here; this neglected retardation correction would increase in importance when electron orbital angular momentum becomes very large (electron distance $r \gg a_0/\alpha$ (α the fine structure constant ~ 137)⁷⁵). We also omit core magnetic effects which are an additive contribution to the dipole-quadrupole polarizability in the work of Buckingham and Longuet-Higgins⁷⁷ and others,^{78–81} because these terms are small for a singlet core at low frequency.^{82,83}

Buckingham and Longuet-Higgins⁷⁷ determine an effective quadrupole origin for optical birefringence measurements by minimizing the size of the first neglected term in the energy. We apply this general principle to optimize the accuracy of a Rydberg effective potential that includes only selected terms, for instance, multipoles through octupole and dipole-dipole polarizability terms, $W \sim 1/r^n$, $n \leq 4$, for which $Q_1^{(A)} = 0$ is a special point.

Expressions for the independent spherical multipole coefficients in Cartesian form for cylindrical symmetry have been given in the literature on electric properties in a number of places, as in the work of Bishop and Maroulis^{60,61} who give results in trigonometric form. Appendix A, Table VII summarizes the polarizability and hyperpolarizability terms in both multipole and trigonometric forms. Symmetry-reduced multipole forms of each polarizability in Equations (5)–(7) were derived from the Cartesian expression by identifying terms equal by symmetry and then evaluating Equation (15) for multipole projection. Reduction to the multipole expansion is used in evaluating different effective potentials, in determining polarizability coefficients from *ab initio* calculations, and in interpreting Rydberg experimental data. We make the same evaluation of polarizability forms for two center potentials, but first consider the origin-independent forms for electric potential.

ORIGIN-INDEPENDENT ELECTRIC MULTIPOLES

Except for the lowest non-zero moment, molecular electric properties depend on the origin and an axis system used to evaluate them. An origin can be assigned based on either electric properties or geometric properties. Origins based on electric properties can be computed from either multipole moments or, in special cases, from polarizabilities as in the effective quadrupole origin.^{77,84,85} Origins based on geometric properties are typically chosen from locations such as atomic positions, the center of mass, or the geometric midpoint of a molecule or bond. Using the rules for the transformation of multipole moments and polarizabilities on the change of origin, special points defined by electric properties can be located if the first few multipoles are known at any other origin. This leads to translational invariants,

values that characterize a static charge distribution without reference to a geometrically defined origin. For cylindrically symmetric charge distributions, the best known invariant of this kind is the quadrupole moment at the center of charge (COC), $Q_2 - Q_1^2/Q_0$, used, for example, in the work of Kay *et al.*,⁸⁶ in analyzing experimental data. For polar molecules, a closer examination shows that the coefficients in a COC expansion can rapidly diverge because the origin is outside the charge distribution, harming the accuracy of the approximation. In addition, when the location of the origin is determined by electric properties of the molecular ion that are not experimentally or theoretically known, the origin must itself be treated as an additional unknown that affects model predictions. This is important since the convergence of the multipole expansion is strongly dependent on the choice of origin.

Origin-independent multipoles for a cylindrically symmetric charge distribution can be described in families. Two families for ions are multipole moments at the center of charge and at the center of dipole.

Multipole moments are transformed along the symmetry axis for linear molecular ions by the formula given by Gray,^{87,88} and in general by the formula given by Stone.⁸⁹ The expression for the effect of a change of origin of multipole moments along an axis of cylindrical symmetry is

$$\begin{aligned} Q_L(z-b) &= \sum_{j=0}^L (-b)^{L-j} \binom{L}{j} Q_j(z) \\ &= \sum_{j=0}^L (-b)^j \binom{L}{j} Q_{L-j}(z). \end{aligned} \quad (19)$$

In this expression, the L -th multipole $Q_L(z)$ is evaluated using as origin the point z along the symmetry axis. The displacement “ b ” is a movement of the reference point (the origin of the multipole expansion) from its initial position by $+b\hat{z}$.

The displacement at which the dipole moment is zero is the center of charge. This is considered to be the effective origin for the potential of a non-rotating molecular ion at a very long range where the energy is represented by the Coulomb term only, since the first omitted term, the dipole, is zero in that origin. To transform multipole moments to the center of charge, the translation from any initial origin, z , is $b = (Q_1(z)/Q_0)$, where $Q_1(z)$ is the dipole moment at z and Q_0 is the ion charge. For an ionically bound diatomic cation, the center of charge is behind the positively charged atom by a distance given by the dipole moment evaluated with the cation as origin. In contrast to non-polar or weakly polar diatomics, the Rydberg electron of an ionically bonded diatomic sees a potential averaged by center-of-mass rotation at long range and is attracted to the center of charge at intermediate distance and then to the cation at short distances. Rotation of the core produces resonances, including scattering from the cation mixing ℓ , formal interaction with dipole-bound levels, and rotation-electronic stroboscopic effects.^{33,90}

Combinations that have the same value using any origin along the symmetry axis, and thus are translationally invariant, are a convenient representation of the electrostatic potential.

TABLE II. Translational invariants in center of charge, ${}_0Q_L$, and center of dipole, ${}_1Q_L$. The distance $b_0 = Q_1(z)/Q_0$ is the distance to the center of charge from any axial location, z . The $b_1 = |\vec{O}_1 - \vec{O}_0| = \pm\sqrt{{}_0Q_2/Q_0}$ distance to the center of dipole is measured from the center of charge. *Ab initio* results for CaF^+ at $R = 3.54 a_0$ taken from a following paper⁹¹ illustrate the divergence of coefficients when an origin outside the molecule is used. Also, see Figure 1.

L	Change of origin	Center of charge	Center of dipole	CaF ⁺	
	$z \rightarrow z - b$	${}_0Q_L = Q_L _{b_0=Q_1/Q_0}$	${}_1Q_L = Q_L _{b_1=\pm\sqrt{{}_0Q_2/Q_0}}$	${}_0Q_L$	${}_1Q_L$
0	$Q_0 \rightarrow Q_0$	Q_0	Q_0	1	1
1	$Q_1 \rightarrow -bQ_0 + Q_1$	0	$-b_1 Q_0$	0	-3.50 (-3.35 expt.)
2	$Q_2 \rightarrow Q_2 - 2bQ_1 + b^2Q_0$	${}_0Q_2 = Q_2 - \frac{Q_1^2}{Q_0}$ $= Q_2 - b_0^2 Q_0$	0	-12.248 (-11.23 expt.)	0
3	$Q_3 \rightarrow Q_3 - 3bQ_2 + 3b^2Q_1 - b^3Q_0$	$Q_3 - 3b_0 Q_2 + 2b_0^3 Q_0$	${}_0Q_3 + 2b_1^3 Q_0$	-90.6	-4.92
4	$Q_4 \rightarrow Q_4 - 4bQ_3 + 6b^2Q_2 - 4b^3Q_1 + b^4Q_0$	$Q_4 - 4b_0 Q_3 + 6b_0^2 Q_2 - 3b_0^4 Q_0$	${}_0Q_4 - 4b_1 {}_0Q_3 - 5b_1^4 Q_0$	-525 (50)	-5.71
5	$Q_5 \rightarrow Q_5 - 5bQ_4 + 10b^2Q_3 - 10b^3Q_2 + 5b^4Q_1 - b^5Q_0$	$Q_5 - 5b_0 Q_4 + 10b_0^2 Q_3 - 10b_0^3 Q_2 + 4b_0^5 Q_0$	${}_0Q_5 - 5b_1 {}_0Q_4 + 10b_1^2 {}_0Q_3 + 9b_1^5 Q_0$	-2800 (200)	-4.4

For an ion, the first set of translationally invariant multipoles is the center-of-charge (COC) moments which are coefficients in an expansion about the center of charge. We represent the center of charge set by ${}_0Q_L$ and the center of charge location by \vec{O}_0 . The dipole term, ${}_0Q_1$, is zero. Since the origin \vec{O}_0 is displaced from any location by the local value of Q_1/Q_0 , the center of charge translation-invariant multipoles for ions is given by the following:

$${}_0Q_L = \underbrace{\sum_{j=0}^L \binom{L}{j} \left(\frac{-Q_1}{Q_0}\right)^j Q_{L-j}}_{\text{evaluate using any origin}} \quad (20)$$

For $L = 1$, ${}_0Q_1 = 0$. The following term in this center of charge expansion is the quadrupole invariant, ${}_0Q_2 = Q_2 - (Q_1^2/Q_0)$, where the dipole and quadrupole may be evaluated using any origin. Invariants through $L = 5$ are given in Table II. The CCSD(T) *ab initio* results shown for $X^1\Sigma^+\text{CaF}^+$ in Table II and experimental results from Kay *et al.*¹⁹ are to be discussed in the following papers.⁹¹ The two following papers both focus on the ground state calcium monofluoride cation. The first paper makes use of the two-center effective potentials to determine for the Ca and F centers, the quenching of dipole-dipole polarizability with bond length due to exchange repulsion and charge overlap. The second paper uses fixed charge *ab initio* calculations to compare and optimize the accuracy of effective

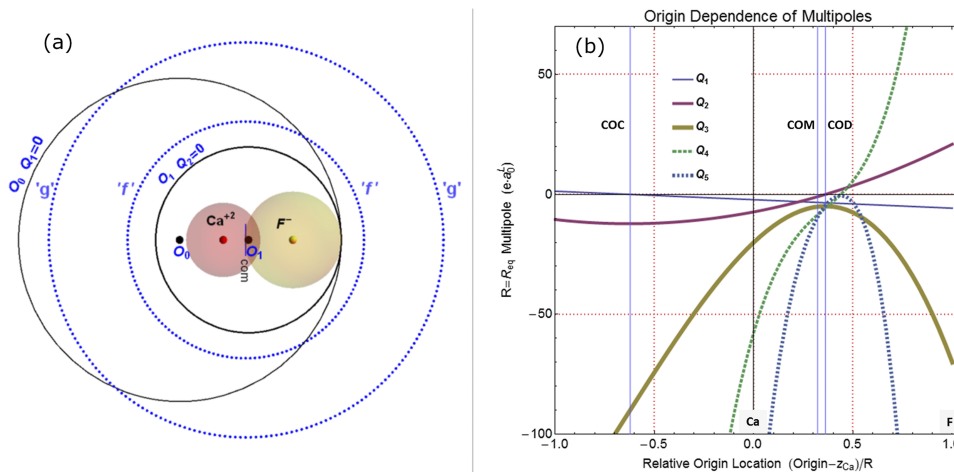


FIG. 1. A multipole representation only converges outside the sphere enclosing the charge distribution. (a) For CaF^+ , circles show the convergence radius for an expansion using the center of charge (O_0) and the center of dipole (O_1), with the center of mass marked. COM inner turning points for “f” and “g” states show that these can be treated as non-penetrating with the center of dipole expansion, but not the center of charge. (b) For dipolar ions, the sensitivity to origin is high. $L = 1-5$ are shown for CaF^+ . Outside a restricted range of origin locations, multipoles rapidly diverge.

potential representations using single center and two center representations.

The center-of-dipole invariants ${}_1Q_L$ are obtained by transforming the center-of-charge moments, ${}_0Q_L$, by applying a displacement $|\vec{O}_1 - \vec{O}_0| = \pm\sqrt{-{}_0Q_2/{}_0Q_0}$ resulting in a series with quadrupole ${}_1Q_2 = 0$. One sign for the displacement is preferred because it gives a new origin between the atoms and a series with much smaller multipole coefficients. The center of dipole invariants for an ion in terms of the center of charge invariants is given by

$${}_1Q_L = \sum_{j=0}^L \binom{L}{j} (\pm\sqrt{-{}_0Q_2/{}_0Q_0})^j {}_0Q_{L-j}. \quad (21)$$

The notation used to this point for the effective multipole expansion and for the translational invariants is summarized in Table IX in Appendix B.

Figure 1(a) based on the electric properties of CaF^+ shows that convergence and interpretation as penetrating or non-penetrating with a single-center multipole expansion depend on the origin. The multipole expansion converges outside of a sphere that encloses the charge distribution, which we approximate by the ionic radii. Circles are drawn at the approximate convergence boundary for \vec{O}_1 (the center of dipole, near COM, zero quadrupole) and \vec{O}_0 (center of charge, behind Ca, zero dipole) expansions. The strong divergence of multipole terms at center of charge and the general origin dependence are illustrated in Figure 1(b) and Table II.

The distinction between penetrating and non-penetrating states of the Rydberg electron has a physical interpretation; states are non-penetrating if the inner turning point of the Rydberg electron is outside the charge density of the molecular ion. From Figures 1(a), 1(d), and 1(f), states are non-penetrating in the center of dipole, but both are penetrating in center of charge, which has been preferred for analysis because of the vanishing dipole moment. However, the determination of electric properties of the molecular ion from a long-range potential depends on the accuracy and convergence properties of the potential. The use of the correct effective potential can allow more states to be treated as non-penetrating by avoiding diverging multipole coefficients in omitted terms.

For a rotating core with the electron at long distance, the appropriate origin is the center of mass so that the dipole is partially or completely rotationally averaged, ultimately reaching the inverse Born-Oppenheimer (IBO) limit.⁹² At a closer approach, the center of charge becomes the point of closest attraction. This effective discontinuity leads to electron-rotational stroboscopic resonances. Accurate representation of the potential in terms of core parameters does not require a specific form or origin and is most useful if the omitted terms are as small as possible so that the physical meaning of parameters is not distorted. Polar molecules, such as CaF^+ , with an *ab initio* center of mass dipole of $-3.3567\text{ e}^-\text{a}_0$, requires explicit treatment of ℓ -mixing in the Zon/Watson Coulomb-dipole basis or in the effective potential. The most accurate analysis of experimental data can explicitly treat ℓ -mixing⁷⁰ and is capable of separate determination of core dipole and quadrupole moments.⁸⁶

For a neutral molecule with a dipole moment, the center of charge is not defined, but the center of dipole and higher centers can be determined. The displacement to the center of dipole in a neutral from an arbitrary location z is $b|_{Q_0=0, Q_1=0} = Q_2(z)/(2Q_1)$. If additional leading moments are zero, $Q_L = 0 \forall L < N$, the position of the zero of Q_{N+1} is displaced from an arbitrary location z , by $b|_{Q_L=0 \forall L < N} = Q_{N+1}(z)/((N+1)Q_N)$. Centers of still higher L are generally multivalued.

Watson⁷⁰ notes that the long-range interaction of the Rydberg electron with the ion core is most simply and accurately represented by a Coulomb series when the origin is the center of charge, since the dipolar term is not present. This is true, but only asymptotically in electron distance, and only for higher orbital angular momentum values. The energy is independent of coordinate origin, so the electrostatic energy can be written as the $(1/r)$ Coulomb term plus the center of charge invariant quadrupole energy, ${}_0Q_2 \frac{C_{2,0}(\Omega)}{r^3}$ to the lowest order, as in the work of Kay *et al.*⁸⁶ Higher order terms can be much larger in the center of charge expansion than in the center of mass. The center of mass is the appropriate origin for the Hamiltonian of the rotating core and for the inclusion of core rotation via the frame transformation of the MQDT quantum defect matrix.^{70,93}

ORIGIN-DEPENDENCE OF POLARIZABILITY COEFFICIENTS

The operators for polarizabilities, given as products of potential derivatives in the Cartesian energy expression, can be transformed in a straightforward manner to a new coordinate system, as in the work of Buckingham (Eq. (5) of Ref. 13). The sum-over-states (SOS) value for the polarizability coefficients is obtained from perturbation theory, with the sum extending over off-diagonal bound and continuum intermediate states,^{40,86} as shown in Appendix A, Table VIII. The SOS contribution from continuum states decreases with molecular size and is reduced by the existence of bound electronic states,⁹⁴ but can be difficult to calculate accurately, as discussed by Jones and Tennyson.⁹⁵ For example, the dipole-dipole polarizability, α , arises from the dipole-moment operator in second order summed over all bound and continuum intermediate states.^{40,95,96} Regardless of computational challenges, the SOS formalism allows the origin dependence of polarizability coefficients to be determined from the origin dependence of off-diagonal matrix elements of the multipole operators. Transformation properties are shown in Appendix A, Table VIII.

It is important to realize that the values of molecular polarizability coefficients depend on the way in which the field is applied (Chap. 9, Stone⁴⁰). This occurs because interactions between polarizable centers differ if the centers feel different external fields. Thus, the molecular polarizability coefficients based on the distributed or multi-center properties are different in a uniform field than in a field which is non-uniform, such as the field from one or more point centers of charge and polarization. The dipole-dipole polarizability for the specific cases of point-charge field and uniform field is compared in

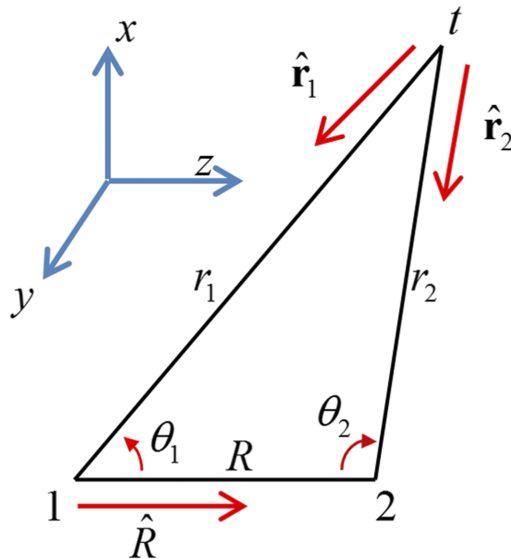


FIG. 2. Coordinate system for 2-center potential models. 1-2 internuclear axis is along z . Centers 1 and 2 have atomic charge and dipole-dipole polarizability but mutual induction can be full or limited. The location of test charge q_t is shown as t . In a multipole expansion, the origin may be at any position along the internuclear axis.

Appendix B. Regardless of these near-field effects on polarizability coefficient values, the change of the coefficients with the origin location is a purely geometric property that remains as given in [Appendix A](#), Table VIII.

Center of polarizability

In analogy with origins at the center of charge, for which the dipole is zero, or the center of dipole, for which the quadrupole is zero, etc., a center of dipole-dipole polarizability can also be defined. The next polarizability term after the $1/r^4$ dipole-dipole term is the $1/r^5$ dipole-quadrupole term ([Appendix A](#), Table VI). There are two types of contributions to the spherical multipole expansion from the dipole-quadrupole (D-Q) interaction ($Q_1^{(A)}, Q_3^{(A)}$) ([Appendix A](#), Table VII), with translation rules in [Appendix A](#), Table VIII. The $Q_1^{(A)}$ contribution is larger and is of lower order and so can be considered as more significant. The $Q_1^{(A)} = 0$ point, which we write as \vec{O}_α , is the center of dipole-dipole polarizability in the sense that the next energy term does not appear or is

minimized. A molecular effective potential based on static multipoles and dipole-dipole polarizability is most accurate in approximating the interaction energy using this origin. This is illustrated quantitatively by *ab initio* data for CaF^+ in a following publication. The dipole-quadrupole polarizability vanishing point, $Q_1^{(A)} = 0$, is always present because the translation rule is linear in displacement ([Appendix A](#), Table VIII). In contrast, the isotropic quadrupole-quadrupole polarizability $Q_0^{(C)}$ variation is quadratic, so the value is often positive regardless of origin.

Table II shows that a series based on electrically determined origins outside the molecule leads to divergent coefficients, while interior points such as \vec{O}_α , center of mass, and midpoint lead to more convergent series. Electrically determined origins introduce the origin location as an additional unknown parameter, except in the extreme asymptotic limit where the hydrogenic treatment is sufficient and detail about the core is lost. This suggests that multi-center or atom-centered geometric potentials are another option for accurate representations, as shown in the section titled Rydberg Two-Center Effective Potentials.

RYDBERG TWO-CENTER EFFECTIVE POTENTIALS

Applied to a molecular ion, the single-center multipole expansions discussed so far have convergence properties that depend on the origin used for the multipole expansion, and the expansion is convergent only outside of a sphere enclosing the charge distribution. An atom or bond-referenced potential does not contain an adjustable origin and may converge outside a multi-sphere volume containing the charge distribution.⁴⁰ However, the accuracy of the effective potential is limited by its faithfulness to the long-range field from the electronic structure of the molecule. This can be tested by relating a multi-center expansion to a single-center multipole expansion using the effective multipole approach, with detailed *ab initio* calculations as a reference. As an initial step in multi-center potentials for Rydberg states, we will base the discussion on the Applequist/Silberstein^{97,98} point-polarizability model, because it is the simplest self-consistent distributed polarizability potential, and because a truncated form of this potential has been applied to Rydberg systems using R-matrix MQDT in a number of publications.

TABLE III. Parallel and perpendicular atomic dipole components in the model with 2 polarizable centers interacting with a test charge. Atomic polarizabilities are allowed to be anisotropic. Subscripts 1 and 2 on r and θ indicate coordinates of the test charge relative to centers 1 and 2, as in Figure 2, with atomic charges Z_1, Z_2 , and test charge, q_t .

Dipole	Truncated potential (AJR)	Self-consistent two-center potential
$\mu_{1,\perp} = \mu_{1,x}$	$-\alpha_{1,\perp} \frac{q_t \sin \theta_1}{r_1^2}$	$\frac{\alpha_{1,\perp}}{f_{R,\perp}} \left(-\frac{q_t \sin \theta_1}{r_1^2} + \frac{q_t \sin \theta_2 \alpha_{2,\perp}}{R^3 r_2^2} \right)$
$\mu_{1,\parallel} = \mu_{1,z}$	$-\alpha_{1,\parallel} \left(\frac{Z_2}{R^2} + \frac{q_t \cos \theta_1}{r_1^2} \right)$	$-\frac{\alpha_{1,\parallel}}{f_{R,\parallel}} \left(\left(\frac{Z_2}{R^2} + \frac{q_t \cos \theta_1}{r_1^2} \right) + \frac{2\alpha_{2,\parallel}}{R^3} \left(\frac{Z_1}{R^2} + \frac{q_t \cos \theta_2}{r_2^2} \right) \right)$
$\mu_{2,\perp} = \mu_{2,x}$	$-\alpha_{2,\perp} \frac{q_t \sin \theta_2}{r_2^2}$	$\frac{\alpha_{2,\perp}}{f_{R,\perp}} \left(-\frac{q_t \sin \theta_2}{r_2^2} + \frac{q_t \sin \theta_1 \alpha_{1,\perp}}{R^3 r_1^2} \right)$
$\mu_{2,\parallel} = \mu_{2,z}$	$\alpha_{2,\parallel} \left(\frac{Z_1}{R^2} + \frac{q_t \cos \theta_2}{r_2^2} \right)$	$\frac{\alpha_{2,\parallel}}{f_{R,\parallel}} \left(\left(\frac{Z_1}{R^2} + \frac{q_t \cos \theta_2}{r_2^2} \right) - \frac{2\alpha_{1,\parallel}}{R^3} \left(\frac{Z_2}{R^2} + \frac{q_t \cos \theta_1}{r_1^2} \right) \right)$
Notation: $f_{R,\perp} \equiv 1 - (\alpha_{1,\perp} \alpha_{2,\perp} / R^6)$ and $f_{R,\parallel} \equiv 1 - (4\alpha_{1,\parallel} \alpha_{2,\parallel} / R^6)$.		

Self-consistent two-center potential (Applequist/Silberstein)

The configuration for a diatomic ion core in the potential from a test charge is shown in Figure 2. If the centers possess dipole polarizability tensors α_1, α_2 , the fields \vec{E}_1, \vec{E}_2 at centers 1 and 2 are

$$\begin{aligned}\vec{E}_1 &= \vec{e}_1 + \mathbf{f}_\mu \alpha_2 \cdot \vec{E}_2, \\ \vec{E}_2 &= \vec{e}_2 + \mathbf{f}_\mu \alpha_1 \cdot \vec{E}_1,\end{aligned}\quad (22)$$

$$\begin{aligned}\mathbf{f}_\mu &= (1/R^3) \text{diag}(-1, -1, 2), \\ \vec{e}_1 &= \frac{q_t}{r_1^2} \begin{pmatrix} -\sin \theta_1 \\ 0 \\ -\cos \theta_1 \end{pmatrix} + \frac{q_2}{R^2} \begin{pmatrix} 0 \\ 0 \\ -1 \end{pmatrix}, \\ \vec{e}_2 &= \frac{q_t}{r_2^2} \begin{pmatrix} -\sin \theta_2 \\ 0 \\ \cos \theta_2 \end{pmatrix} + \frac{q_1}{R^2} \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}.\end{aligned}\quad (23)$$

The fields \vec{e}_1, \vec{e}_2 are the Coulomb fields from the test charge and the adjacent atom. This is a linear system with the following solution for the resulting fields at the atomic centers:

$$\begin{aligned}\vec{E}_1 &= \left(\mathbf{I} - \tilde{\mathbf{f}}_\mu \alpha_2 \tilde{\mathbf{f}}_\mu \alpha_1 \right)^{-1} \left(\vec{e}_1 + \tilde{\mathbf{f}}_\mu \alpha_2 \vec{e}_2 \right), \\ \vec{E}_2 &= \left(\mathbf{I} - \tilde{\mathbf{f}}_\mu \alpha_1 \tilde{\mathbf{f}}_\mu \alpha_2 \right)^{-1} \left(\vec{e}_2 + \tilde{\mathbf{f}}_\mu \alpha_1 \vec{e}_1 \right).\end{aligned}\quad (24)$$

The atom-centered dipole moments are then

$$\vec{\mu}_1 = \alpha_1 \vec{E}_1, \text{ and } \vec{\mu}_2 = \alpha_2 \vec{E}_2. \quad (25)$$

The expressions for the atomic dipole moments from Equations (24) and (25), allowing anisotropic atomic polarizabilities, are shown in Table III in the column labeled as self-consistent two-center potential.

The Rydberg effective potential omits test-charge independent terms in the electric interaction energy. The atomic dipole part of the potential, H_{dipole} , is the integral at each center of the dipole-field energy as the test charge magnitude is varied from zero to its final value, q_t . The fields \vec{E}_j are those of Equation (24),

$$\begin{aligned}H_{2\text{ctr}} &= H_{\text{Coul}} + H_{\text{dipole}}, \\ H_{\text{Coul}} &= \frac{q_t Z_1}{r_1} + \frac{q_t Z_2}{r_2}, \\ \frac{\partial H_{\text{dipole}}}{\partial \vec{E}} &= -\vec{\mu}(\vec{E}) = -\alpha(\vec{E}) \cdot \vec{E}, \\ H_{\text{dipole}} &= - \sum_j \int d\vec{E}_j^T \cdot \vec{\mu}_j \\ &= - \sum_j \int_0^{q_t} dq \frac{d\vec{E}_j(q)}{dq} \cdot \alpha_j(q) \cdot \vec{E}_j(q).\end{aligned}\quad (26)$$

If the atomic polarizabilities are assumed to depend on a fixed internuclear separation, R , but to be independent of the electron position, then $\alpha_j(q)$ may be replaced by α_j , and the two-center energy can be written in terms of the two-center

dipole moments shown in Table III as follows:

$$\begin{aligned}H_{2\text{ctr}}|_{\alpha_j(q)=\alpha_j} &= H_{\text{Coul}} - \frac{1}{2} \sum_j \vec{E}_j(q)^T \cdot \alpha_j \cdot \vec{E}_j(q) \Big|_0^{q_t} \\ &= H_{\text{Coul}} - \frac{1}{2} \sum_j \vec{\mu}_j(q)^T \cdot \alpha_j^{-1} \cdot \vec{\mu}_j(q) \Big|_0^{q_t}.\end{aligned}\quad (27)$$

As pointed out by Raab,⁹⁹ the third line of Equation (26) is Equation (3) of Buckingham,¹³ where the dipole-dipole polarizability, α , is given an expansion in field and field derivatives. Taking atomic polarizabilities to be independent of the test charge position while allowing a parametric dependence on internuclear separation, R , is an approximation. It may be justified for an ionically bonded core, since the field of the nearby atom is larger than that from the Rydberg electron, which is assumed to spend most time outside the charge distribution. However, *hyperpolarizabilities of the molecular ion are zero when atomic polarizabilities do not depend on the electron position*, because polarization energy is then only quadratic in the field from the electron.

Atomic polarizability dependence on bond length R is critically necessary because the electric field from the opposing ion varies with R , and the Pauli and Coulomb repulsions from the opposing electron cloud also vary with R , leading to polarizability quenching which is an important feature of molecular mechanics and other applications. These quenching effects are consistent with the reduction of anion polarizabilities from free space values observed in a crystal¹⁰⁰ and provide an alternative to polarizability quenching models used in molecular mechanics^{1,101,102} based on quantum chemistry calculations. Since we are focusing on polar systems, we also treat each of the centers as originating from a particular ionic configuration (see Chap. VI.4(b) in Herzberg¹⁰³), neglecting charge-transfer polarizability effects, which are described in Stone's monograph.⁴⁰

Truncated two-center potential

A potential which has been used in several previous publications on polar diatomic is a truncated form of this potential, omitting the polarizing effect of feedback from induced dipoles. In a ground-breaking 1997 paper, Arif, Jungen, and Roche¹⁴ proposed a one-electron effective potential for polar diatomic Rydberg states and applied it to Rydberg states of CaF and BaF, both of which are effective one-electron systems. This AJR potential has been applied in MQDT calculations for rare-gas hydrides,^{53,54} CaCl,¹⁵ BaI,¹⁶ and CaF,^{17,104} allowing comparison to quantum-defect matrices derived from Rydberg experimental data.¹⁹ The AJR potential, excluding core de-shielding terms, uses Coulomb, atomic polarization, and dipole energy terms in a way that is equivalent to the following expression:

$$\begin{aligned}H_{\text{AJR}} &= \left(H_{\text{Coul}} - \frac{1}{2} \vec{e}_1^T \tilde{\mu}_1 - \frac{1}{2} \vec{e}_2^T \tilde{\mu}_2 \right. \\ &\quad \left. + \frac{1}{R^3} (\tilde{\mu}_1 \cdot \tilde{\mu}_2 - 3\tilde{\mu}_{1,z} \cdot \tilde{\mu}_{2,z}) \right) \Big|_0^{q_t},\end{aligned}\quad (28)$$

where $\tilde{\mu}_1 = \alpha_1 \vec{e}_1$ and $\tilde{\mu}_2 = \alpha_2 \vec{e}_2$.

TABLE IV. Series expansions in powers of $(1/R)$ of molecular ion properties from the two-center potentials show that inclusion of feedback from the dipole field changes terms involving the $\alpha_1\alpha_2$ product of atomic polarizabilities, doubling the leading coefficients in dipole-dipole and dipole-quadrupole anisotropy ($Q_2^{(\alpha)}$ and $Q_3^{(\alpha)}$). Angle-averaged values such as $Q_0^{(\alpha)}$ and $Q_1^{(A)}$, and the quadrupole invariant others are less affected. Atomic charges are Z_1, Z_2 , axial positions, z_1, z_2 . Exact forms for a more complete list are given in [Appendix B](#).

$Q_L^{(S)}$	AJR	Self-consistent
Dipole-dipole polarizability		
$Q_0^{(\alpha)} = \bar{\alpha}/2$	$\frac{1}{2}(\alpha_1 + \alpha_2)$	$AJR + \frac{3\alpha_1\alpha_2(\alpha_1 + \alpha_2)}{R^6} + \frac{8\alpha_1^2\alpha_2^2}{R^9} + \dots$
$Q_2^{(\alpha)} = \frac{\Delta\alpha}{3}$	$\frac{2\alpha_1\alpha_2}{R^3}$	$AJR + \frac{2\alpha_1\alpha_2}{R^3} + \frac{3\alpha_1\alpha_2(\alpha_1 + \alpha_2)}{R^6} + \dots$
Dipole-quadrupole polarizability		
$Q_1^{(A)}$	$2(\alpha_1 z_1 + \alpha_2 z_2) + \frac{2\alpha_1\alpha_2(z_1 + z_2)}{5R^3}$	$AJR + \frac{2\alpha_1\alpha_2(z_1 + z_2)}{5R^3} + \dots$
$Q_3^{(A)}$	$\frac{18\alpha_1\alpha_2(z_1 + z_2)}{5R^3}$	$AJR + \frac{18\alpha_1\alpha_2(z_1 + z_2)}{5R^3} + \dots$
Quadrupole invariant (COC): $^{(1)}\tilde{Q}_2 = Q_2 - (Q_1^2/Q_0)$		
$Q_2^{(0)}Q_0^{(0)} - Q_1^{(0)2} = \Theta_{zz}^{(0)}q_t^{(0)} - \mu_z^{(0)2}$	$R^2Z_1Z_2 + \frac{2Z_2^2\alpha_1 + 2Z_1^2\alpha_2}{R} - \frac{Z_2^2\alpha_1^2 + 6Z_1Z_2\alpha_1\alpha_2 + Z_1^2\alpha_2^2}{R^4} + \dots$	$AJR - \frac{8Z_1Z_2\alpha_1\alpha_2}{R^4} + \dots$

The dipole moment values are those of Table III and depend on the value of the test charge, q_t . Fields \vec{e}_1, \vec{e}_2 are given in Equation (23) and include only direct fields, omitting the additional fields and polarization from induced dipoles. Mutual induction is omitted, but the first-order dipole-dipole energy between the induced dipoles is added separately. Expressions for the dipole moments $\vec{\mu}_1, \vec{\mu}_2$ computed from this potential are given in Table III for comparison with the self-consistent forms. Because mutual induction enhances an inline head-to-tail arrangement of dipoles and suppresses the transverse parallel arrangement, polarization anisotropy is higher in the full two-center potential than in the AJR potential as shown in Table IV and [Appendix B](#). Polarizability anisotropy in both potentials is always positive. We refer to (28) as the AJR potential, but the expression given in Arif, Jungen, and Roche¹⁴ differs from Equation (28) in three ways: short-range atom-centered polarizability cutoff functions are introduced, an ℓ -dependent core de-shielding pseudo-potential is used at the cation, and Rydberg energy units are used rather than the atomic units used here.

The induced dipole moments for the self-consistent two-center and the truncated energy expressions in Table III can be used with Equation (27) or (28) to define effective potentials for the Rydberg electron. In Table III, the atomic polarizabilities parallel and perpendicular to the diatomic axis are allowed to differ. It is important to note that the dependence of the atomic dipole moment components on test charge magnitude, and thus on field, is not more than linear. This occurs because atomic polarizabilities have been given no dependence on electron position r , although a parametric dependence is allowed on internuclear distance, R , an assumption that results in *zero values for molecular hyperpolarizabilities*.

The potential of Equation (28), augmented by core-desielding terms as given in the work of Arif *et al.*,¹⁴ has been used to solve the Rydberg-electron Schrödinger equation by multi-channel quantum defect theory (MQDT) to obtain quantum defects for Rydberg series for alkaline earth monohalides, and other diatomics. Agreement with experimental results has been reasonably good, although discrepancies have been noted

in a recent global QDT fit of the experimental dataset for CaF Rydberg states.¹⁹ The discrepancies have been especially significant in the dependence on inter-nuclear separation, R . Our following publication on $X^1\Sigma^+ \text{CaF}^+$ ⁹¹ shows that there is a strong variation in the fluorine anion polarizability with R .

Example: $X^1\Sigma^+ \text{BaF}^+$

$X^1\Sigma^+ \text{BaF}^+$, the ion core of BaF Rydberg states, is a highly polar ion that has been studied in a number of experimental^{105–108} and theoretical¹⁴ publications, but not yet been the subject of a numerical QDT/frame transformation modeling

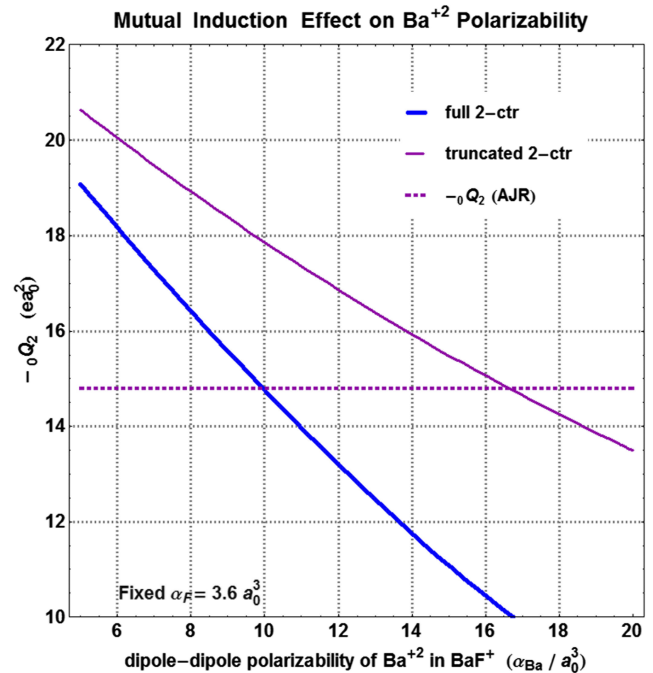


FIG. 3. The estimated atomic polarizability of Ba^{+2} in BaF^+ is $10 a_0^3$ with full mutual induction and $16.5 a_0^3$ in the model without mutual induction based on matching the horizontal line for the estimated value quadrupole invariant of $-14.78 e a_0^2$. Experimental values for Ba^{+2} are in the range of $10.5\text{--}10.75 a_0^3$.^{3,29} A value of $3.6 a_0^3$ for the ionically bonded F^- polarizability is used. See text for further discussion.

TABLE V. Origin dependence of multipoles and polarizabilities for BaF^+ at $R_{\text{eq}} = 3.93 a_0$. Polarization reduces the multipole moments from the ionic point charge values which were given in the work of Jakubek and Field. Arif *et al.* atomic polarizabilities were used in the AJR potential to determine the quadrupole invariant, ${}_0Q_2$, which was then matched by full 2-center potential by smaller atomic polarizabilities, relying on the lower ${}_0Q_2$ sensitivity to the model seen in Table IV. The full model predicts a greater molecular polarizability anisotropy $\Delta\alpha/\bar{\alpha}$. Series limited to $(1/r^4)$ terms have small coefficients for the omitted terms if expanded at CO α or COD. The center of polarizability approximately divides the internuclear distance in proportion to the estimated atomic polarizabilities. Assumed values are shown bold-underlined. Values true by definition at the particular origin are bold.

BaF potential						
Origin	Ionic charges		Full 2-center			
	COM	AJR COM	COM	CO α (\vec{O}_α)	COD (\vec{O}_1)	COC (\vec{O}_0)
$z\text{-ZBa}$		0.476	0.476	1.077	1.664	-2.65
$(\alpha(\text{Ba}), \alpha(\text{F}))$	(0,0)	(11.4, 4.7)		(10.0, 3.6)		
${}_0Q_2, r^{-3}$ ($Q_2 - Q_1^2/Q_0$)	-30.9	-14.78		-14.76		
$\Delta\alpha/\bar{\alpha}$	NA	0.33		0.61		
$(Q_0^{(\alpha)}, Q_2^{(\alpha)}), r^{-4}$	(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

of the rovibronic spectrum as has been done for CaF .¹⁹ Arif, Jungen, and Roche chose atomic polarizability parameters for the truncated two center potential for both CaF and BaF on the basis of agreement with experimental quantum defects. The CaF^+ values result in a value for the center of charge quadrupole invariant at the equilibrium R , ${}_0Q_2 = Q_2 - Q_1^2/Q_0$, that is quite close to that predicted from all-electron *ab initio* calculations.⁹¹ To illustrate the role of mutual induction in the effective potential in BaF^+ , we use the AJR atomic polarizabilities (11.4 (Ba^{+2}), 4.7 (F^-), Table II¹⁴), thereby determining the value of the quadrupole invariant to be ${}_0Q_2^{\text{BaF}^+} = -14.78 e a_0^2$ (see Appendix B, Equations (B5) and (B6)). The full two-center model is adjusted to match these values by varying the atomic polarizabilities. In order to determine the Ba^{+2}

polarizability, the F^- polarizability is fixed at a value determined for F^- in CaF^+ ($3.6 a_0^3$).⁹¹ In support of this equivalence, we note that the calculation in the work of Field and Gittins¹⁰⁹ shows similar (70% ^1S /30% ^1P) F^- molecular orbital compositions at equilibrium for both CaF^+ and BaF^+ . Figure 3 shows the quadrupole invariant predicted by the full and the truncated potentials as a function of Ba^{+2} atomic polarizability evaluated at the equilibrium R . A much smaller value of Ba polarizability ($10 a_0^3$) is needed in the full potential than in the truncated potential to match the predicted quadrupole invariant ($-14.78 a_0^3$), because of polarization enhancement by dipole-dipole mutual induction. Experimental values for Ba^{+2} in the same atomic units are close to the full potential value, in the range of 10.1–10.75.^{3,29,110}

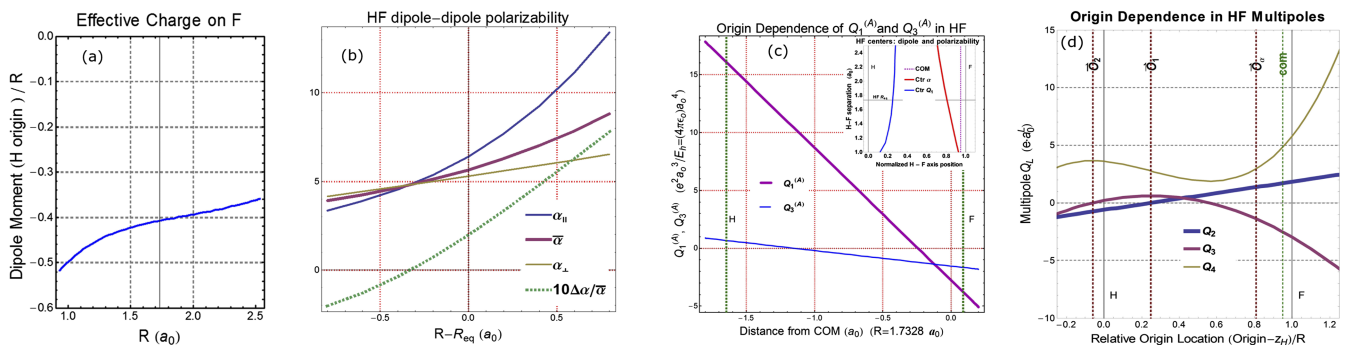


FIG. 4. Origin and geometry dependence of electric properties of neutral hydrogen fluoride based on Maroulis.¹¹² Panel (a) shows the effective charge on F to be nearly constant with R , indicating polarizability increasing with R . Panel (b) shows the polarizability increasing with R . The change in anisotropy sign marks a change from molecular to atomic behavior discussed in the text. Buldakov *et al.*¹²⁴ find a peak parallel polarizability of $28 a_0^3$ at about $4.3 a_0$, before decreasing for separated neutrals. Panel (c) shows the graphical determination of the center of polarizability ($Q_1^{(A)} = 0$). The inset shows center variation with bond length. Panel (d) shows multipole moment variation with origin.

The variation of moments and polarizabilities with origin and with atomic polarizability values is shown in Table V. The results calculated for the potential of Equation (28) are labeled AJR because it matches the ex-core part of the AJR potential and the AJR atomic polarizabilities were used. The predicted anisotropy of the dipole-dipole polarizability in the full potential is nearly double that of the truncated potential. It is recognized that the mutual polarization, and therefore the anisotropy, can be over-estimated by the full dipole-induced dipole model,⁴⁰ but no experimental data are yet available for polarizability anisotropy in the alkaline-earth fluoride cations.

Example: Potential of neutral HF

Although the HF monomer does not form a stable anion,¹¹¹ the interaction of neutral HF with external charges and fields is also described by a multipole and polarizability expansion that has convergence properties that depend on the origin. HF is an ionic molecule by Herzberg's criteria, with the ionic curve crossing at $3.4 a_0$ (double the equilibrium bond length of $1.7 a_0$) and the ionic radius of F^- at $2.2 a_0$ being less than 1.5 the bond length. In addition, HF shows, through the polarizability anisotropy, a transition from a longer R regime which can be modeled by the two center model to a short R region which is more consistent with a molecular picture in which the proton penetrates and perturbs the F^- ion, as in the ligand field model of Rice, Martin, and Field. Some of the electrical properties of HF as a function of origin and bond length are based on the extensive *ab initio* results in the work of Maroulis.¹¹²

Figure 4(a) shows an effective charge on the fluorine which varies little over the $\pm 0.8 a_0$ range shown. In the two-center model of an A-B diatomic ion or neutral, an approximation to the polarization-modified charge on B is the origin-A dipole moment divided by the internuclear separation R,

$$\begin{pmatrix} Q_0 \\ Q_1(z_A)/R \\ Q_2(z_A)/R^2 \end{pmatrix} = \begin{pmatrix} Z_A + Z_B \\ \frac{Q_{1,A} + Q_{1,B}}{R} + Z_B \\ \frac{Q_{2,A} + Q_{2,B}}{R^2} + \frac{2Q_{1,B}}{R} + Z_B \end{pmatrix} \cong \begin{pmatrix} Z_A + Z_B \\ Z_B + \frac{Q_{1,A} + Q_{1,B}}{R} \\ Z_B + \frac{2Q_{1,B}}{R} \end{pmatrix} \\ = \begin{pmatrix} Z_A + Z_B \\ Z_B + \frac{Z_B \alpha_A}{R^3} + \frac{Z_A \alpha_B}{R^3} \\ Z_B + \frac{2Z_A \alpha_B}{R^3} \end{pmatrix} \quad (29)$$

The rightmost expression for Q_1/R and Q_2/R^2 also gives a glimpse of why values of α_A and α_B can be derived from the values for Q_1 and Q_2 . Because the effective charge on F in HF is constant or decreasing with R while the field from H is decreasing, the polarizability of F^- must be increasing. Since the assignment of polarizability to hydrogen, especially in a bond predicted to be ionic is uncertain, and anticipating results to be reported for CaF^+ , the variation is assignable to F^- when the dipole and quadrupole values are analyzed using the full potential.⁹¹

Figure 4(b) shows that the parallel polarizability and anisotropy are increasing especially rapidly, due to the preference for the aligned dipole orientation. However, beginning at $0.3 a_0$ below the equilibrium bond length, the polarizability anisotropy becomes negative, a result which is impossible in the dipole-induced dipole model. In this region, the molecule

is not ionically bonded, but is better described as a proton embedded in the F^- electron density. Negative polarizability anisotropy indicates that the distortable electrons are molecular rather than atomic or ionic in character. For boron hydride (BH),¹¹³ which is less polar than HF, the transition to negative anisotropy occurs almost exactly at the equilibrium bond length. Neutral CaF is regarded as a Rydberg molecule even down to its ground state, and as a result, the outer electron is molecular in character, not atomic. The CaF polarizability anisotropy is strongly negative,^{36,114} $\Delta\alpha/\bar{\alpha} = -0.6$ due to the fact that the unpaired electron is back-polarized, residing behind the metal ion which resists pulling the electron away along the axis. An atoms-in-molecules approach is not useful for covalent or electrically diffuse systems.

The potential or the force-field of HF is most convergent when the single center form is truncated after the named center term. The center of polarizability \tilde{O}_α is defined by $Q_1^{(A)} = 0$, determined as shown in Figure 4(c), with the variation in position of center of dipole and center of polarizability with bond length shown in the inset, and the origin dependence in Figure 4(d). The center of polarizability potential is the balanced representation of the potential experienced by external charges that includes terms through $(1/r^4)$ by including multipole moments through the octupole and the dipole-dipole polarizability, referenced to a point near the polarizability center.

DISCUSSION

Rydberg states may be analyzed by a QDT-frame transformation approach using a matrix of quantum defects and derivatives with respect to energy and geometry, for the non-rotating system, followed by a frame transformation to model the entire set of levels of the system including rotation and vibration.^{18,19,93} The states may also be modeled by an effective Hamiltonian approach in which subsets of the experimental data are analyzed to obtain physically meaningful parameters, such as the center of mass dipole, invariant quadrupole, and polarizabilities of the ion core.^{86,115} An example of the first approach is found in the global treatment of CaF s-p-d-f levels by Kay *et al.*,¹⁹ to determine the invariant quadrupole and average polarizability of the CaF^+ core.^{18,93} An example of the second approach is the use of a long-range model in Kay *et al.*,⁸⁶ based on the methods used for ArH Rydberg states by Dabrowski *et al.*^{115–117} Jungen and Roche¹¹⁸ had shown earlier that a QDT matrix approach is able to represent the entire ArH spectrum. The different strengths of the two approaches are evident. In the QDT case, the entire spectrum is represented, but simple electric parameters of the core are not directly obtained, while with an effective potential, physically meaningful molecular parameters are determined but the full dynamics is not represented.

In this paper, we focus on optimizing effective potentials for use in Rydberg R-matrix calculations,^{17,104,119} as a faithful representation of charge/molecular-ion interactions, and as a predictive tool for moments and polarizabilities. We have shown in Figure 1 how the origin chosen for a single-center multipole series affects the convergence properties of a multipole series, and the transition from

penetrating to non-penetrating in the representation of Rydberg states. The method can be applied to any diatomic or polyatomic with a cylindrically symmetric ion core. With the improvement in resolution available from the application of microwave methods to Rydberg states, the extension of this approach to non-cylindrically symmetric ion core molecules such as CaO is interesting and is being explored. For less ionic systems, more general distributed polarizability and charge flow models⁴⁰ are also an option for the Rydberg spectroscopy of chemically important molecules observed at high resolution.

Two variants of a two-center potential have been considered, a truncated form and a self-consistent form with a very long history, the first of which has previously been used in modeling quantum defects for a range of polar Rydberg diatomics. Multi-center potentials are useful for Rydberg states of polar molecules in the intermediate range where the core rotational structure cannot be averaged because of the presence of core-Kepler stroboscopic resonances,^{33,90} and where the internal structure leads to shape resonances.¹⁰⁴ The difference between the truncated and the full two-center potentials is two-fold: molecular anisotropy predictions are larger in the full form, as in Table V for BaF⁺, and inferred atomic polarizabilities are smaller in the full model than in the truncated model. The full form is consistent with the Silberstein/Applequist/Thole approach often used in MM and QM/MM.

Ab initio calculations can be used in several different ways to assist in evaluating effective potentials and in interpreting experimental data. The core dipole and quadrupole moments in the two center potentials are shown in Table V or in Appendix B and depend solely on the atomic dipole polarizabilities. As a result, *ab initio* dipole and quadrupole moment functions of the isolated ion are sufficient to completely specify the two-center potential at a particular internuclear distance. The two center potential matching the dipole and quadrupole captures the asymmetry through the dipole and symmetry through the quadrupole of the core charge distribution and provides estimates of the effect of charge and exchange repulsion

through reduced atomic dipole polarizabilities. The potential also predicts *R*-dependent values for molecular polarizabilities of all second-order types, with hyperpolarizabilities excluded due to an assumption in the derivation. These can be compared to experimental values and to *ab initio* predictions from fixed charge/finite field configurations (Refs. 61, 120, and 121, Equation (15)) and can be used to develop model-free estimates of polarizability. The additional radial dependence of the effective moment isolates each polarizability coefficient and allows them to be determined from an approximation in powers of $1/r$.

In a third approach, the *ab initio* point charge energies themselves can be approximated with a single center multipole series, including static multipoles and selected polarizability coefficients. The multipole coefficients have the origin dependence that we have discussed, but the parallel and perpendicular dipole polarizability coefficients are origin independent. The approximation from the two-center potential can be compared to the single-center multipole series and to the *ab initio* point data. This is illustrated in a following paper for CaF⁺.⁹¹

The improved potential form and analyses demonstrated in this work provide a deep understanding of atomic polarizabilities in ionic bonds and constrained environments, in estimating molecular properties from experimental data, and in highly accurate predictions. Furthermore, the effective potentials can be improved or elaborated in response to new experimental results. The need for an analysis of high resolution Rydberg data from new chirped-pulse microwave methods^{122,123} motivates a closer examination of these effective potentials and a comparison with *ab initio* calculations, focusing on polarizability and ionic bonding in the ion core.

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APPENDIX A: ELECTRIC PROPERTIES OF A CYLINDRICALLY SYMMETRIC CHARGE DISTRIBUTION

Appendix A consists of the group of tables which describe the symmetry and electric properties of a cylindrically symmetric charge distribution. Table VI gives the number of independent coefficients for different polarizability terms. Table VII describes polarization energies. Table VIII provides the rules for change of origin. Tables IX and X summarize the notation used in this paper.

TABLE VI. Number of independent parameters in interaction of a point charge with a cylindrically symmetric charge distribution for terms up to 4 potential derivatives. Except for the dipole-octupole coefficient ($E_{\alpha,\beta\gamma\delta}$), these results are well known. Odd L terms are of negative parity and so contribute to ℓ -mixing, and also contribute in traveling-wave interactions such as bulk birefringence, while energy contributions are first order in the ℓ -mixed Coulomb-dipole basis or off-diagonal in the hydrogenic basis.

$C_{\infty,v}$	Static multipole	Contributing to even $L, M = 0$					Contributing to odd $L, M = 0$	
	$Q_L^{(0)}$	$\alpha_{\alpha\beta}$	$C_{\alpha\beta,\gamma\delta}$	$E_{\alpha,\beta\gamma\delta}$	$\gamma_{\alpha\beta\gamma\delta}$	$B_{\alpha,\beta,\gamma\delta}$	$A_{\alpha,\beta\gamma}$	$\beta_{\alpha\beta\gamma}$
Independent parameters	1	2	3	2	3	4	2	2
L	L	0,2	0,2,4	2,4	0,2,4	0,2,4	1,3	1,3
r power dependence	$-(L+1)$	-4	-6	-6	-8	-7	-5	-6

TABLE VII. Multipole and polarizability energies for a cylindrically symmetric charge distribution in a point charge potential. Terms with dipole (D), quadrupole (Q), and octupole (O) factors are shown in multipole series form and in trigonometric form. The trigonometric forms are equivalent to those given by Bishop and Maroulis. Both effective multipole and trigonometric forms require the factor under radial, and the multipole form requires a factor of $C_{L,0}(\theta, 0) = P_L(\cos \theta)$ according to the L subscript in $Q_L^{(S)}$. The “Notation” column translates abbreviated forms to Cartesian subscripts.

Energy	Radial	Multipole form/ $P_L(\cos \theta)$	Trigonometric form	Notation
Static core $Q_L^{(0)}$	$\frac{q_t}{r^{L+1}}$	$Q_L^{(0)}$ core multipole	$Q_L^{(0)} P_L(\cos \theta)$	
DD α	$-\frac{q_t^2}{r^4}$	$Q_0^{(\alpha)} = (2a_1 + a_2)/6$ $Q_2^{(\alpha)} = (a_2 - a_1)/3$	$\frac{1}{2} (a_1 \sin^2 \theta + a_2 \cos^2 \theta)$	$a_1 = \alpha_{xx} = \alpha_{\perp}$ $a_2 = \alpha_{zz} = \alpha_{\parallel}$
DQ A	$-\frac{q_t^2}{r^5}$	$Q_1^{(A)} = 2(2A_1 + A_2)/5$ $Q_3^{(A)} = (3A_2 - 4A_1)/5$	$\cos \theta \left(\frac{2A_1 \sin^2 \theta}{4} + \frac{A_2}{4} (3 \cos 2\theta + 1) \right)$	$A_1 = A_{x,xz} = A_{\perp}$ $A_2 = A_{z,zz} = A_{\parallel}$
DO E	$-\frac{q_t^2}{r^6}$	$Q_2^{(E)} = (3e_2 - 8e_1)/7$ $Q_4^{(E)} = 4(2e_1 + e_2)/7$	$\frac{e_1}{2} (-3 - 5 \cos 2\theta) \sin^2 \theta$ $+ \frac{e_2}{2} (5 \cos^2 \theta - 3) \cos^2 \theta$	$e_1 = E_{xxxx}$ $e_2 = E_{zzzz}$
QQ C	$-\frac{q_t^2}{r^6}$	$Q_0^{(C)} = (8c_1 + c_2 + 8c_6)/10$ $Q_2^{(C)} = (-8c_1 + 5c_2 + 4c_6)/7$ $Q_4^{(C)} = 12(c_1 + 2c_2 - 4c_6)/35$	$\frac{3}{2} \begin{pmatrix} c_1 \sin^4 \theta \\ + c_2 \cos^2 \theta \cos 2\theta \\ + 4c_6 \sin^2 \theta \cos^2 \theta \end{pmatrix}$	$c_1 = C_{xx,xx}$ $c_2 = C_{zz,zz}$ $c_6 = C_{xz,xz}$
DDD β	$\frac{q_t^3}{r^6}$	$Q_1^{(\beta)} = (2\beta_1 + \beta_2)/10$ $Q_3^{(\beta)} = (\beta_2 - 3\beta_1)/15$	$\left(\frac{\beta_1}{2} \sin^2 \theta + \frac{\beta_2}{6} \cos^2 \theta \right) \cos \theta$	$\beta_1 = \beta_{xxz}$ $\beta_2 = \beta_{zzz}$
DDQ B	$\frac{q_t^3}{r^7}$	$Q_0^{(B)} = (4b_1 + b_2 + b_4 + 4b_6)/15$ $Q_2^{(B)} = (-16b_1 + 11b_2 + 2b_4 + 8b_6)/42$ $Q_4^{(B)} = (4b_1 + 6b_2 - 4b_4 - 16b_6)/35$	$\frac{1}{4} \begin{pmatrix} 2b_1 + 3b_2 \\ -2b_4 - 8b_6 \end{pmatrix} \cos^4 \theta$ $+ \frac{1}{4} \begin{pmatrix} -4b_1 - b_2 \\ +2b_4 + 8b_6 \end{pmatrix} \cos^2 \theta$ $+ b_1/2$	$b_1 = B_{x,x,xx}$ $b_2 = B_{z,z,zz}$ $b_4 = B_{x,x,zz}$ $b_6 = B_{x,z,xz}$
DDDD γ	$-\frac{q_t^4}{r^8}$	$Q_0^{(\gamma)} = (8g_1 + 3g_2 + 12g_4)/360$ $Q_2^{(\gamma)} = (-4g_1 + 3g_2 + 3g_4)/126$ $Q_4^{(\gamma)} = (g_1 + g_2 - 6g_4)/105$	$(g_1/24) \sin^4 \theta$ $+ (g_2/24) \cos^4 \theta$ $+ (g_4/16) \sin^2 2\theta$	$g_1 = \gamma_{xxxx}$ $g_2 = \gamma_{zzzz}$ $g_4 = \gamma_{xxzz}$

APPENDIX B: ENERGY TERMS IN PERTURBATION THEORY AND TWO-CENTER EFFECTIVE POTENTIAL

For a cylindrically symmetric charge distribution interacting with a point charge, the multipole expansion including polarizability terms has the following form:

$$(4\pi\epsilon_0) W(\mathbf{r}) = \sum_L q_t Q_L(r, q_t) \left(\frac{C_{L,0}(\theta, \varphi)}{r^{L+1}} \right). \quad (\text{B1})$$

The perturbation expansion of the multipole coefficients combines polarizabilities of different types,

$$q_t Q_L(r, q_t) = q_t Q_L^{(0)} - \sum_{S,L \text{ with } Q_L^{(S)} \neq 0} (-1)^{n_S} q_t^{n_S} \frac{Q_L^{(S)}}{r^{k_{SL}}}. \quad (\text{B2})$$

The exact forms of the polarizability coefficients $Q_L^{(S)}$ in the two-center truncated or self-consistent potentials can be factored as in (B3), with terms up to quadratic in the atomic dipole-dipole polarizability coefficients. (The expression for the origin-invariant quadrupole $\Theta - (\mu^2/q)$ requires powers up to 4.) Units of dipole-dipole polarizability in atomic units are $e^2 a_0^2 / E_h = (4\pi\epsilon_0) a_0^3 \sim a_0^3$. For simplicity, the $(4\pi\epsilon_0)$ will be omitted because its numerical value is 1 in atomic units, so the units of dipole-dipole polarizability are taken to be a

volume, while the second order polarizabilities of L1-L2 type have units $a_0^{L1+L2+1}$. Isotropic atomic polarizabilities are shown because anisotropy has not been found to improve agreement with *ab initio* results,

$$Q_L^{(S)} = \left(1 \alpha_1 / R^3 \alpha_1^2 / R^6 \right) \mathbf{M}^{(S,L)} \left(1 \alpha_2 / R^3 \alpha_2^2 / R^6 \right)^T. \quad (\text{B3})$$

The factors $f_{R,p}, f_{R,a}$ appearing in the tables are

$$f_{R,p} \equiv 1 - (\alpha_1 \alpha_2 / R^6), \quad (\text{B4})$$

$$f_{R,a} \equiv 1 - (4\alpha_1 \alpha_2 / R^6).$$

Z_1, Z_2 are charges, and z_1, z_2 are z-coordinates of the centers, $z_2 = z_1 + R$.

Static multipole moments

Static multipole moments are shown in Table XI.

Dipole-dipole polarizability

Dipole-dipole terms are shown in Table XII. Polarizability coefficients depend on the way in which the field is applied. Table XIII compares the dipole-dipole polarizability coefficients in the uniform field and the point charge cases. Units of dipole-dipole polarizability in atomic units are $e^2 a_0^2 / E_h = (4\pi\epsilon_0) a_0^3 \sim a_0^3$.

TABLE VIII. Translational properties of the polarizabilities of a cylindrically symmetric charge distribution. All polarizabilities that include only dipole operators are origin independent ($\alpha, \beta, \gamma, Q_0^\alpha, Q_2^\alpha$). The point at which $Q_1^{(A)}$ is zero is a polarizability-determined origin that optimizes the accuracy of a multipole + dipole polarizability expansion.

Term (radial factor)	Matrix element	Change on $z \rightarrow z - a$
Any off-diagonal matrix element of the dipole operator $\hat{Q}_1 (r^{-2})$	$\langle i \hat{Q}_1 j \rangle \Big _{i \neq j}$	$\rightarrow \langle i -aQ_0 + Q_1 j \rangle \Big _{j \neq i}$ $= -aQ_0 \langle i j \rangle \Big _{j \neq i} + \langle i Q_1 j \rangle \Big _{j \neq i}$ $= \langle i Q_1 j \rangle \Big _{j \neq i}$ since Q_0 is scalar.
Dipole polarizability, hyperpolarizability α, β, γ (r^{-4}, r^{-6}, r^{-8})	$\alpha_{\alpha\beta} \sim \sum_{j \neq i} \frac{\langle i \hat{\mu}_\alpha j \rangle \langle j \hat{\mu}_\beta i \rangle + \text{c.c.}}{\Delta E_{ij}}$ (3rd, 4th order for β, γ)	No change
Dipole-quadrupole $A_{\alpha, \beta\gamma} (r^{-5})$	$\sum_{j \neq i} \frac{\langle i \hat{\mu}_\alpha j \rangle \langle j \hat{\Theta}_{\beta\gamma} i \rangle + \text{c.c.}}{\Delta E_{ij}}$	$\delta A_{x,xz} = -\frac{3}{2} a \alpha_{xx}; \delta A_{z,zz} = -2a \alpha_{zz}$ $\delta Q_1^{(A)} = -a (4Q_0^{(\alpha)} - (2/5) Q_2^{(\alpha)});$ $\delta Q_3^{(A)} = - (18a Q_2^{(\alpha)} / 5)$
Quadrupole-quadrupole $C_{\alpha\beta, \gamma\delta} (r^{-6})$	$\sum_{j \neq i} \frac{\langle i \hat{\Theta}_{\alpha\beta} j \rangle \langle j \hat{\Theta}_{\gamma\delta} i \rangle + \text{c.c.}}{\Delta E_{ij}}$	$\delta C_{xx,xx} = -\frac{3}{2} a A_{z,zz} + a^2 \alpha_{zz}$ $\delta C_{zz,zz} = -3a A_{z,zz} + 4a^2 \alpha_{zz}$ $\delta C_{xz,xz} = -\frac{9}{2} a A_{x,xz} + \frac{9}{4} a^2 \alpha_{xx}$ $\delta Q_0^{(C)} = -\frac{21}{5} a Q_1^{(A)} + \frac{3}{10} a Q_3^{(A)}$ $+ 6a^2 Q_0^{(\alpha)} + \frac{3}{5} a^2 Q_2^{(\alpha)}$
Dipole-octupole $E_{\alpha, \beta\gamma\delta} (r^{-6})$	$\sum_{j \neq i} \frac{\langle i \hat{\mu}_\alpha j \rangle \langle j \hat{\Omega}_{\beta\gamma\delta} i \rangle + \text{c.c.}}{\Delta E_{ij}}$	$\delta E_{x,xxx} = 3a A_{x,xz} - \frac{3}{2} a^2 \alpha_{xx}$ $\delta E_{z,zzz} = -\frac{9}{2} a A_{z,zz} + 3a^2 \alpha_{zz}$
Dipole-dipole-quadrupole $B_{\alpha, \beta\gamma\delta} (r^{-7})$	Third order perturbation theory	$\delta B_{x,x,xx} = a \beta_{xxz}; \delta B_{z,z,zz} = -2a \beta_{zzz}$ $\delta B_{x,x,zz} = -2a \beta_{xxz}; \delta B_{x,z,xz} = -\frac{3}{2} a \beta_{xxz}$

TABLE IX. Notation for the effective moment expansion and invariants of a cylindrically symmetric charge distribution.

Notation	Description
Q_L	M = 0 multipole moment, origin unspecified
$Q_L(z)$	Multipole moment of a charge distribution evaluated with origin at position z along the axis of symmetry
$Q_L(r, q)$	Effective multipole moment of order L in the presence of charge q at radial distance r. The radial dependence is due to polarization by the charge
$Q_L^{(0)}$	Multipole moment of order L of the unperturbed charge distribution
$Q_L^{(S)}$	Contribution of polarizability of type S to effective multipole moments of spherical harmonic L, where S is one of the polarizability types $\alpha, \beta, \gamma, \delta, A, B, C, E, \dots$. Values depend on origin following the translation rules in Appendix A , Table VIII
${}_0Q_L, \vec{O}_0$	Pre-subscript 0 on ${}_0Q_L$, and subscript 0 on \vec{O}_0 indicates center of charge
${}_1Q_L, \vec{O}_1$	Pre-subscript 1 on ${}_1Q_L$, and subscript 1 on \vec{O}_1 indicates center of dipole

TABLE X. Notation in 2-center potentials.

2-center potential	Notation
Atomic charges (e)	Z_1, Z_2
Atomic positions (a_0)	z_1, z_2
Atomic dipole-dipole polarizabilities (a_0^3)	α_1, α_2
Interatomic distance (a_0)	$R = z_2 - z_1$

The dipole-dipole polarizability is origin-independent. This is shown for these effective potentials by the absence of atomic coordinates, z_1, z_2 in these expressions.

Difference between uniform-field and test-charge for dipole-dipole polarizability

Table XIII shows that polarizability coefficients depend on the way in which the fields are applied and are not a pure property of the charge distribution (Chap. 9, Stone⁴⁰). In order to illustrate this environmental dependence, we contrast the point-charge-perturbed dipole-dipole polarizability just given with the uniform-field Applequist-Silberstein dipole-dipole polarizability from Chap. 8 of the Stone monograph⁴⁰, rearranged to match our current format.

In Table XIII, there are three notable differences between uniform-field and point-charge-field interaction: (1) there are

TABLE XI. Two-center potential static multipole moments.

Static multipole moments		
$M^{(S,L)}$ for $Q_L^{(S)}$ (Perturbation theory)	AJR potential	Self-consistent two-center potential
$M^{(0,0)}$ for $Q_0^{(0)} = Q_{\text{total}}$	$Z_1 + Z_2$	$Z_1 + Z_2$
$M^{(0,1)}$ $Q_1^{(0)} = \mu_z^{(0)}$	$\begin{pmatrix} z_1 Z_1 + z_2 Z_2 & RZ_1 & 0 \\ -RZ_2 & 2R(Z_1 - Z_2) & 0 \\ 0 & 0 & 0 \end{pmatrix}$	$\begin{pmatrix} z_1 Z_1 + z_2 Z_2 & Rf_{R,a}^{-2} Z_1 & 0 \\ -Rf_{R,a}^{-2} Z_2 & 4Rf_{R,a}^{-2} (Z_1 - Z_2) & 4Rf_{R,a}^{-2} Z_1 \\ 0 & -4Rf_{R,a}^{-2} Z_2 & 0 \end{pmatrix}$
$M^{(0,2)}$ $Q_2^{(0)} = \Theta_{zz}^{(0)}$	$\begin{pmatrix} z_1^2 Z_1 + z_2^2 Z_2 & 2z_2 RZ_1 & 0 \\ -2z_1 RZ_2 & 4R(z_1 Z_1 - z_2 Z_2) & 0 \\ 0 & 0 & 0 \end{pmatrix}$	$\begin{pmatrix} z_1^2 Z_1 + z_2^2 Z_2 & 2z_2 Rf_{R,a}^{-2} Z_1 & 0 \\ -2z_1 Rf_{R,a}^{-2} Z_2 & 8Rf_{R,a}^{-2} (z_1 Z_1 - z_2 Z_2) & 8z_2 Rf_{R,a}^{-2} Z_1 \\ 0 & -8z_1 Rf_{R,a}^{-2} Z_2 & 0 \end{pmatrix}$
$M^{(0,3)}$ $Q_3^{(0)} = \Omega_{zzz}^{(0)}$	$\begin{pmatrix} z_1^3 Z_1 + z_2^3 Z_2 & 3z_2^2 RZ_1 & 0 \\ -3z_1^2 RZ_2 & 6R(z_1^2 Z_1 - z_2^2 Z_2) & 0 \\ 0 & 0 & 0 \end{pmatrix}$	$\begin{pmatrix} z_1^3 Z_1 + z_2^3 Z_2 & 3z_2^2 Rf_{R,a}^{-2} Z_1 & 0 \\ -3z_1^2 Rf_{R,a}^{-2} Z_2 & 12Rf_{R,a}^{-2} (z_1^2 Z_1 - z_2^2 Z_2) & 12z_2^2 Rf_{R,a}^{-2} Z_1 \\ 0 & -12z_1^2 Rf_{R,a}^{-2} Z_2 & 0 \end{pmatrix}$
$M^{(0,4)}$ $Q_4^{(0)} = \Phi_{zzzz}^{(0)}$	$\begin{pmatrix} z_1^4 Z_1 + z_2^4 Z_2 & 4z_2^3 RZ_1 & 0 \\ -4z_1^3 RZ_2 & 8R(z_1^3 Z_1 - z_2^3 Z_2) & 0 \\ 0 & 0 & 0 \end{pmatrix}$	$\begin{pmatrix} z_1^4 Z_1 + z_2^4 Z_2 & \frac{4z_2^3 Rf_{R,a}^{-2} Z_1}{R^2 f_{R,a}^2} & 0 \\ -4z_1^3 Rf_{R,a}^{-2} Z_2 & 16Rf_{R,a}^{-2} (z_1^3 Z_1 - z_2^3 Z_2) & 16z_2^3 Rf_{R,a}^{-2} Z_1 \\ 0 & -16z_1^3 Rf_{R,a}^{-2} Z_2 & 0 \end{pmatrix}$

no dependences on the squares of the atomic polarizabilities in the uniform field case; (2) the divergence factors $f_{R,a}, f_{R,p}$ appear linearly in the uniform field results, but quadratically in the point charge results; and (3) the anisotropy term proportional to the $\alpha_1 \alpha_2$ product in the uniform field case is half that in the point charge case. The point charge perturbation results in a more non-symmetric polarizability than the uniform field.

Dipole-quadrupole (A)

Table XIV gives the expressions for the dipole-quadrupole effective moments.

Quadrupole-quadrupole (C) and dipole-octupole polarizability (E)

Table XV gives the expressions for the quadrupole-quadrupole and dipole-octupole polarizabilities. Table I shows that some of these terms cannot be distinguished with a point charge perturbation.

Quadrupole invariant of a cylindrically symmetric molecular ion

The center of charge quadrupolar invariant is given by Eq. (B5). It is independent of coordinate origin, as shown by the absence of atomic coordinates in the following equations:

TABLE XII. Dipole-dipole polarizability in point charge field.

Dipole-dipole polarizability (point-charge perturbation)		
$M^{(S,L)}$ for $Q_L^{(S)}$	AJR	Full two center potential
$\frac{\mathbf{M}^{(\alpha,0)}}{R^3}$ for $Q_0^{(\alpha)} = \bar{\alpha}/2$	$\frac{1}{2} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & \frac{1}{2} \left(\frac{1}{3f_{R,a}^2} + \frac{2}{3f_{R,p}^2} \right) & 0 \\ \frac{1}{2} \left(\frac{1}{3f_{R,a}^2} + \frac{2}{3f_{R,p}^2} \right) & \frac{4}{3R^3} \left(\frac{1}{f_{R,a}^2} - \frac{1}{f_{R,p}^2} \right) & \frac{1}{3R^3} \left(\frac{2}{f_{R,a}^2} + \frac{1}{f_{R,p}^2} \right) \\ 0 & \frac{1}{3R^3} \left(\frac{2}{f_{R,a}^2} + \frac{1}{f_{R,p}^2} \right) & 0 \end{pmatrix}$
$\frac{\mathbf{M}^{(\alpha,2)}}{R^3}$ for $Q_2^{(\alpha)} = \frac{\Delta\alpha}{3}$	$2 \begin{pmatrix} 0 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & \frac{1}{3} \left(\frac{1}{f_{R,a}^2} - \frac{1}{f_{R,p}^2} \right) & 0 \\ \frac{1}{3} \left(\frac{1}{f_{R,a}^2} - \frac{1}{f_{R,p}^2} \right) & \frac{4}{R^3} \left(\frac{2}{3f_{R,a}^2} + \frac{1}{3f_{R,p}^2} \right) & \frac{1}{3R^3} \left(\frac{4}{f_{R,a}^2} - \frac{1}{f_{R,p}^2} \right) \\ 0 & \frac{1}{3R^3} \left(\frac{4}{f_{R,a}^2} - \frac{1}{f_{R,p}^2} \right) & 0 \end{pmatrix}$

TABLE XIII. Difference in dipole-dipole polarizability between uniform field and point-charge field interaction.

Excitation-dependence of dipole-dipole polarizability		
$M^{(S,L)}$ for $Q_L^{(S)}$	Uniform-field interaction	Point-charge interaction (repeated from previous table)
$\frac{\mathbf{M}^{(\alpha,0)}}{R^3}$ for $Q_0^{(\alpha)} = \bar{\alpha}/2$	$\frac{1}{2} \begin{pmatrix} 0 & \frac{1}{3f_{R,a}} + \frac{2}{3f_{R,p}} & 0 \\ \frac{1}{3f_{R,a}} + \frac{2}{3f_{R,p}} & \frac{1}{3R^3} \left(\frac{4}{f_{R,a}} - \frac{4}{f_{R,p}} \right) & 0 \\ 0 & 0 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & \frac{1}{2} \left(\frac{1}{3f_{R,a}^2} + \frac{2}{3f_{R,p}^2} \right) & 0 \\ \frac{1}{2} \left(\frac{1}{3f_{R,a}^2} + \frac{2}{3f_{R,p}^2} \right) & \frac{1}{3R^3} \left(\frac{4}{f_{R,a}^2} - \frac{4}{f_{R,p}^2} \right) & \frac{1}{3R^3} \left(\frac{2}{f_{R,a}^2} + \frac{1}{f_{R,p}^2} \right) \\ 0 & \frac{1}{3R^3} \left(\frac{2}{f_{R,a}^2} + \frac{1}{f_{R,p}^2} \right) & 0 \end{pmatrix}$
$\frac{\mathbf{M}^{(\alpha,2)}}{R^3}$ for $Q_2^{(\alpha)} = \frac{\Delta\alpha}{3}$	$\frac{1}{3} \begin{pmatrix} 0 & \left(\frac{1}{f_{R,a}} - \frac{1}{f_{R,p}} \right) & 0 \\ \left(\frac{1}{f_{R,a}} - \frac{1}{f_{R,p}} \right) & \frac{1}{R^3} \left(\frac{4}{f_{R,a}} + \frac{2}{f_{R,p}} \right) & 0 \\ 0 & 0 & 0 \end{pmatrix}$	$\frac{1}{3} \begin{pmatrix} 0 & \left(\frac{1}{f_{R,a}^2} - \frac{1}{f_{R,p}^2} \right) & 0 \\ \left(\frac{1}{f_{R,a}^2} - \frac{1}{f_{R,p}^2} \right) & \frac{2}{R^3} \left(\frac{4}{f_{R,a}^2} + \frac{2}{f_{R,p}^2} \right) & \frac{1}{R^3} \left(\frac{4}{f_{R,a}^2} - \frac{1}{f_{R,p}^2} \right) \\ 0 & \frac{1}{R^3} \left(\frac{4}{f_{R,a}^2} - \frac{1}{f_{R,p}^2} \right) & 0 \end{pmatrix}$

$$-{}_0Q_2 Q_0 = -(Q_0 Q_2 - Q_1^2) = \left(1 \frac{\alpha_1}{R^3} \left(\frac{\alpha_1}{R^3} \right)^2 \left(\frac{\alpha_1}{R^3} \right)^3 \left(\frac{\alpha_1}{R^3} \right)^4 \right) \mathbf{M}^{(DQ)} \left(1 \frac{\alpha_2}{R^3} \left(\frac{\alpha_2}{R^3} \right)^2 \left(\frac{\alpha_2}{R^3} \right)^3 \left(\frac{\alpha_2}{R^3} \right)^4 \right)^T. \quad (\text{B5})$$

The absence of atomic positions, z_1, z_2 , in the following expressions indicate origin independence.

Truncated (AJR) potential (exact form for M , and series expansion for invariant)

$$\mathbf{M}_{\text{AJR}}^{(DQ)} = R^2 \begin{pmatrix} -Z_1 Z_2 & -2Z_1^2 & Z_1^2 \\ -2Z_2^2 & 6Z_1 Z_2 & 4Z_1 (Z_1 - Z_2) \\ Z_2^2 & -4Z_2 (Z_1 - Z_2) & 4(Z_1 - Z_2)^2 \end{pmatrix}, \quad (\text{B6})$$

$$\begin{aligned} -{}_0Q_{2,AJR} Q_0 = & -R^2 Z_1 Z_2 + \frac{-2Z_2^2 \alpha_1 - 2Z_1^2 \alpha_2}{R} + \frac{Z_2^2 \alpha_1^2 + 6Z_1 Z_2 \alpha_1 \alpha_2 + Z_1^2 \alpha_2^2}{R^4} \\ & + \frac{-4Z_1 Z_2 \alpha_1^2 \alpha_2 + 4Z_2^2 \alpha_1^2 \alpha_2 + 4Z_1^2 \alpha_1 \alpha_2^2 - 4Z_1 Z_2 \alpha_1 \alpha_2^2}{R^7} + \dots \end{aligned} \quad (\text{B7})$$

TABLE XIV. Dipole-quadrupole polarizability.

Dipole-quadrupole polarizability		
$M^{(S,L)}$ for $Q_L^{(S)}$	AJR	Full two-center potential
$\frac{\mathbf{M}^{(A,1)}}{R^3}, Q_1^{(A)} = -\frac{2(A_{\parallel} + 2A_{\perp})}{5}$	$2 \begin{pmatrix} 0 & z_2 & 0 \\ z_1 & (z_1 + z_2)/5 & 0 \\ 0 & 0 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & \frac{4z_2}{5f_{R,a}^2} + \frac{6z_2}{5f_{R,p}^2} & 0 \\ \frac{4z_1}{5f_{R,a}^2} + \frac{6z_1}{5f_{R,p}^2} & \left(\frac{16z_1}{5R^3 f_{R,a}^2} + \frac{16z_2}{5R^3 f_{R,a}^2} \right) - \frac{12z_1}{5R^3 f_{R,p}^2} - \frac{12z_2}{5R^3 f_{R,p}^2} & \frac{16z_2}{5R^6 f_{R,a}^2} + \frac{6z_2}{5R^6 f_{R,p}^2} \\ 0 & \frac{16z_1}{5R^6 f_{R,a}^2} + \frac{6z_1}{5R^6 f_{R,p}^2} & 0 \end{pmatrix}$
$\frac{\mathbf{M}^{(A,3)}}{R^3}, Q_3^{(A)} = -\frac{3A_{\parallel} - 4A_{\perp}}{5}$	$18 \begin{pmatrix} 0 & 0 & 0 \\ 0 & (z_1 + z_2)/5 & 0 \\ 0 & 0 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & \frac{6z_2}{5f_{R,a}^2} - \frac{6z_2}{5f_{R,p}^2} & 0 \\ \frac{6z_1}{5f_{R,a}^2} - \frac{6z_1}{5f_{R,p}^2} & \left(\frac{24z_1}{5R^3 f_{R,a}^2} + \frac{24z_2}{5R^3 f_{R,a}^2} \right) + \frac{12z_1}{5R^3 f_{R,p}^2} + \frac{12z_2}{5R^3 f_{R,p}^2} & \frac{24z_2}{5R^6 f_{R,a}^2} - \frac{6z_2}{5R^6 f_{R,p}^2} \\ 0 & \frac{24z_1}{5R^6 f_{R,a}^2} - \frac{6z_1}{5R^6 f_{R,p}^2} & 0 \end{pmatrix}$

TABLE XV. Quadrupole-quadrupole and dipole-octupole polarizabilities.

Quadrupole-quadrupole (C) and dipole-octupole polarizability (E)		
$M^{(S,L)}$ for $Q_L^{(S)}$	AJR	Full two-center potential
$\mathbf{M}^{(C,0)}/R^3$ $Q_0^{(C)} =$ $\frac{2C_{xx,xx} + C_{zz,zz}}{5}$ $+\frac{2C_{xy,xy} + 4C_{xz,xz}}{5}$ $= \frac{1}{5} \sum_{\alpha\beta} C_{\alpha\beta,\alpha\beta} \equiv C$	$\begin{pmatrix} 0 & z_2^2 & 0 \\ z_1^2 & \frac{2z_1z_2}{5} & 0 \\ 0 & 0 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & \frac{2z_2^2}{5f_{R,a}^2} + \frac{3z_2^2}{5f_{R,p}^2} & 0 \\ \frac{2z_1^2}{5f_{R,a}^2} + \frac{3z_1^2}{5f_{R,p}^2} & \frac{16z_1z_2}{5R^3f_{R,a}^2} - \frac{12z_1z_2}{5R^3f_{R,p}^2} & \frac{8z_2^2}{5R^6f_{R,a}^2} + \frac{3z_2^2}{5R^6f_{R,p}^2} \\ 0 & \frac{8z_1^2}{5R^6f_{R,a}^2} + \frac{3z_1^2}{5R^6f_{R,p}^2} & 0 \end{pmatrix}$
$\mathbf{M}^{(C+E,2)}/R^3$ $Q_2^{(C)} + Q_2^{(E)} =$ $-\frac{4(C_{xx,xx} - C_{zz,zz})}{7}$ $-\frac{4(C_{xy,xy} - C_{xz,xz})}{7}$ $+\frac{8E_{x,xxx} - 3E_{z,zzz}}{7}$	$\begin{pmatrix} 0 & 4z_2^2 & 0 \\ 4z_1^2 & \frac{6z_1^2 + 10z_1z_2 + 6z_2^2}{7} & 0 \\ 0 & 0 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & \frac{13z_2^2}{7f_{R,a}^2} + \frac{15z_2^2}{7f_{R,p}^2} & 0 \\ \frac{13z_1^2}{7f_{R,a}^2} + \frac{15z_1^2}{7f_{R,p}^2} & \left(\frac{36z_1^2}{7R^3f_{R,a}^2} + \frac{32z_1z_2}{7R^3f_{R,a}^2} \right) & \frac{52z_2^2}{7R^6f_{R,a}^2} + \frac{15z_2^2}{7R^6f_{R,p}^2} \\ 0 & \left(\frac{12z_1z_2}{7R^3f_{R,p}^2} - \frac{24z_2^2}{7R^3f_{R,p}^2} \right) & 0 \end{pmatrix}$
$\mathbf{M}^{(C+E,4)}/R^3$ $Q_4^{(C)} + Q_4^{(E)} =$ $\frac{3(4C_{xx,xx} + 17C_{zz,zz})}{70}$ $+\frac{12(C_{xy,xy} - 8C_{xz,xz})}{70}$ $+\frac{4(2E_{x,xxx} + E_{z,zzz})}{7}$	$\begin{pmatrix} 0 & 0 & 0 \\ 0 & 36\frac{(5z_1^2 + 6z_1z_2 + 5z_2^2)}{35} & 0 \\ 0 & 0 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & \frac{96z_2^2}{35f_{R,a}^2} - \frac{96z_2^2}{35f_{R,p}^2} & 0 \\ \frac{96z_1^2}{35f_{R,a}^2} - \frac{96z_1^2}{35f_{R,p}^2} & \left(\frac{48z_1^2}{7R^3f_{R,a}^2} + \frac{288z_1z_2}{35R^3f_{R,a}^2} \right) & \frac{384z_2^2}{35R^6f_{R,a}^2} - \frac{96z_2^2}{35R^6f_{R,p}^2} \\ 0 & \left(\frac{48z_2^2}{7R^3f_{R,a}^2} + \frac{24z_1^2}{7R^3f_{R,p}^2} \right) & 0 \end{pmatrix}$

Self-consistent potential (exact form (B8) and series expansion (B9))

$$\mathbf{M}^{(DQ)} = \begin{pmatrix} -R^2Z_1Z_2 & -\frac{2Z_1^2}{Rf_{R,a}^2} & \frac{Z_1^2}{R^4f_{R,a}^4} & 0 & 0 \\ -\frac{2Z_2^2}{Rf_{R,a}^2} & \frac{2Z_1Z_2(-1+8f_{R,a}^2)}{R^4f_{R,a}^4} & -\frac{8Z_1(-Z_1+Z_2+Z_1f_{R,a}^2)}{R^7f_{R,a}^4} & \frac{8Z_1^2}{R^{10}f_{R,a}^4} & 0 \\ \frac{Z_2^2}{R^4f_{R,a}^4} & -\frac{8Z_2(Z_1-Z_2+Z_2f_{R,a}^2)}{R^7f_{R,a}^4} & \frac{16(Z_1^2-3Z_1Z_2+Z_2^2)}{R^{10}f_{R,a}^4} & \frac{32Z_1(Z_1-Z_2)}{R^{13}f_{R,a}^4} & \frac{16Z_1^2}{R^{16}f_{R,a}^4} \\ 0 & \frac{8Z_2^2}{R^{10}f_{R,a}^4} & -\frac{32(Z_1-Z_2)Z_2}{R^{13}f_{R,a}^4} & -\frac{32Z_1Z_2}{R^{16}f_{R,a}^4} & 0 \\ 0 & 0 & \frac{16Z_2^2}{R^{16}f_{R,a}^4} & 0 & 0 \end{pmatrix}, \quad (\text{B8})$$

$$-(Q_1^2 - Q_2Q_0) = -R^2Z_1Z_2 - 2(Z_2^2\alpha_1 + Z_1^2\alpha_2)/R^1 + (Z_2^2\alpha_1^2 + 14Z_1Z_2\alpha_1\alpha_2 + Z_1^2\alpha_2^2)/R^4 \\ - 8\alpha_1\alpha_2(2Z_2^2\alpha_1 + 2Z_1^2\alpha_2 + Z_1Z_2(\alpha_1 + \alpha_2))/R^7 + \dots \quad (\text{B9})$$

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