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# Complete basis set extrapolated potential energy, dipole, and polarizability surfaces of alkali halide ion-neutral weakly avoided crossings with and without applied electric fields

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Complete basis set extrapolations of alkali halide (LiF, LiCl, NaF, NaCl) energy, dipole, and polarizability surfaces are performed with and without applied fields along the internuclear axis using state-averaged multireference configuration interaction. Comparison between properties (equilibrium separation, dissociation energy, crossing distance, diabatic coupling constant, dipole, and polarizability) derived from the extrapolated potential energy (or dipole) surfaces are made with those obtained from direct extrapolation from the basis set trends. The two extrapolation *procedures* are generally found to agree well for these systems. Crossing distances from this work are compared to those of previous work and values obtained from the Rittner potential. Complete basis set extrapolated crossing distances agree well with those derived from the Rittner potential for LiF, but were significantly larger for LiCl, NaF, and NaCl. The results presented here serve as an important set of benchmark data for the development of new-generation many-body force fields that are able to model charge transfer. © 2004 American Institute of Physics. [DOI: 10.1063/1.1690232]

## I. INTRODUCTION

Application of high-level quantum methods to fundamental types of molecular interactions leads to an increased understanding of the forces between interacting molecules, and fuels the development of more computationally tractable *quantitative* models that can be applied efficiently to larger chemical systems and over a broader range of configurational space. Current-generation “molecular mechanical” force fields almost uniformly rely on quantum chemical calculations for at least part of their parametrization.<sup>1–4</sup> Some force fields use quantum mechanical calculations almost exclusively to determine molecular mechanical parameters.<sup>5</sup> Others put forth considerable effort to adjust, in addition, a relatively small number of parameters based on bulk simulations, albeit for mixtures of only a few components.<sup>6</sup>

A promising class of next-generation force fields are those based on the principle of *chemical potential equalization*,<sup>7–9</sup> which are derivable from density functional theory assuming a *smooth* Taylor series expansion of the density functional to second order in the density response. A challenging test for new-generation models is the treatment of charge transfer. Studies employing statistical mechanical arguments<sup>10,11</sup> and charge-constrained electronic structure methods<sup>12</sup> suggest that a smooth energy model may not be adequate to accurately describe charge transfer events.

Gas phase alkali halides represent a set of prototypical systems to study charge transfer and have been the subject of numerous theoretical<sup>13–32</sup> and experimental<sup>33–37</sup> studies. These systems are dominated by ionic character at close separation and are well characterized as neutral atoms at

large separation. The two lowest  $^1\Sigma^+$  states undergo an avoided crossing at some distance (referred to as the crossing *distance*) and is marked by a sharp change in the dipole moment of the system. The crossing distances of alkali halide systems are fairly large ( $\approx 13.7$ – $17.8$  bohr) and can be estimated from a simple few experimentally measurable quantities atomic/ionic properties (see EPAPS supplementary material<sup>38</sup>). A commonly applied approximate relationship for the crossing distance  $R_c$  (in the absence of applied fields) can be derived from the Rittner potential,<sup>14,15,28</sup> and is given by

$$R_c = \frac{1}{\Delta E_\infty} + \frac{\alpha_{M^+} + \alpha_{X^-}}{2R_c^3 \Delta E_\infty}, \quad (1)$$

where  $\alpha_{M^+}$  and  $\alpha_{X^-}$  are the alkali metal ( $M^+$ ) and halide ( $X^-$ ) ion polarizabilities, respectively, and  $\Delta E_\infty$  is the difference between the asymptotic values of the energy of the neutral and ionic states at infinite separation, i.e.,  $\Delta E_\infty = IP(M) - EA(X)$  where  $IP(M)$  is the ionization potential of the alkali metal and  $EA(X)$  is the electron affinity of the halogen. The crossing distance  $R_c$  appears on both sides of Eq. (1), and hence is solved iteratively (Note: atomic units are used here, and consequently the units of charge do not appear explicitly.) Discussion of a more general model for the energy difference of diabatic states and crossing distance in the presence of an applied field is provided as supplementary material.<sup>38</sup>

A purpose of this work is to provide highly accurate benchmark adiabatic potential energy, dipole, and polarizability surfaces for LiF, LiCl, NaF, and NaCl with and without application of external electric fields. These properties serve as an important set of benchmarks for prototypical electron transfer systems, and can be used to develop and test

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many-body force fields that include new models for charge transfer.

A large amount of attention has been spent on the prediction of properties in the limit of a complete basis set (CBS) based on extrapolation,<sup>39–66</sup> including studies with particular emphasis on the prediction of equilibrium geometries.<sup>42,46,53–55,57,67</sup> The CBS procedure most commonly employed involves the determination of a particular property value at a series of basis sets that form a systematic hierarchy, and use those calculated values to directly extrapolate to the basis set limit. However, many properties are related to the potential energy surface (PES) or its derivatives (such as the dipole surface). Consequently, an alternate procedure is to determine the CBS extrapolated PES, from which an estimate of the property values in the CBS limit can be derived. The latter procedure was found to provide highly accurate rotational and vibrational spectroscopic observables for NaH and NaD.<sup>58</sup> A purpose of this work is to analyze the degree to which these two procedures produce similar predictions for property values in the CBS limit in application to alkali halide systems.

Work involving the extrapolation of entire PESs has been performed,<sup>55,58,61,68</sup> and have the most relevance for applications to reaction dynamics and the design of new-generation quantum models for molecular simulations. Some attention has been spent on the extrapolation of nonenergetic surfaces such as dipole moment and polarizability<sup>58</sup> and on the extrapolation of entire ground and excited state PESs.<sup>61</sup> Alkali halide dimers in the gas phase exhibit a weakly avoided crossing and require special attention when extrapolating adiabatic surfaces (energetic, dipole, etc.) in the region of the crossing distance. The extrapolation of alkali halide adiabatic data on a grid of internuclear separation is not reliable; the avoided crossing is sensitive to basis set and causes significant changes in the behavior of the surfaces. A purpose of this work is to further the extrapolation procedures used by others<sup>55,58,61,68</sup> to determine CBS extrapolated ground and excited state adiabatic potential, dipole, and polarizability surfaces for alkali halide systems.

Curve crossing events of alkali halide systems have been well-studied with theoretical methods in the past. Bauschlicher and Langhoff<sup>13</sup> examined the energies and dipole moments of LiF using full configuration interaction (FCI), complete active space self consistent field (CASSCF), multireference configuration interaction (MRCI), state-averaged CASSCF (SA-CASSCF) using equal weights for the ionic and neutral solutions, and MRCI based on SA-CASSCF optimized orbitals, notated here as SA-MRCI. The authors found FCI to produce smooth dipole surfaces and CASSCF and MRCI to contain discontinuities. The discontinuities were found to vanish when a state averaging process was used in the CASSCF procedure, but the result predicted crossing distances that were systematically too small when compared to values derived from the Rittner potential.<sup>14</sup>

Sousa *et al.*<sup>14</sup> studied the electric field effects of LiF, LiCl, NaF, and NaCl using the then recently developed<sup>69</sup> multistate complete active space second-order perturbation theory (MS-CASPT2) and compared crossing distances to a modified form of the Rittner potential. The crossing distance

as approximated through the modified Rittner potential [Eq. (2) of Sousa *et al.*<sup>14</sup>] takes into consideration applied electric fields and was found to agree reasonably well with the MS-CASPT2 results. The authors found a LiF crossing distance closer to that predicted by the Rittner potential than, but still close to the SA-MRCI prediction of Bauschlicher and Langhoff.<sup>13</sup>

Werner and Meyer<sup>15</sup> have noted the importance of being able to reproduce the quantity  $\Delta E_\infty$  in order to calculate reasonable values of the crossing distance. Both Sousa *et al.*<sup>14</sup> and Bauschlicher and Langhoff<sup>13</sup> took great care in their choice of basis, but still calculated LiF crossing distances slightly smaller than those derived from the Rittner potential using experimental values for the ionization energy and electron affinity. In the present study, CBS extrapolations may be useful in resolving discrepancies in the predicted and calculated crossing distances.

The outline of the paper follows: Section II describes the *ab initio* calculations and CBS extrapolations used in this work. Section III discusses the calculation results and compares the two applied CBS extrapolation procedures with each other and with results reported previously in the literature. Section IV concludes by summarizing the results of the paper.

## II. METHODS

### A. *Ab initio* reference data

*Ab initio* calculations were performed on LiF, LiCl, NaF, and NaCl at 70 internuclear separations with  $-0.0005$ ,  $0.0000$ , and  $0.0005$  a.u. fields along the internuclear axis. The orientation of the molecule relative to the applied electric field is such that the negative field stabilizes the neutral state and the positive field stabilizes the ionic state. This orientation was chosen to conform with those used in related studies.<sup>14</sup> SA-CASSCF calculations were performed with equal weighting of the two lowest  $^1\Sigma^+$  states. The active space used to construct the SA-CASSCF wave function consists of eight orbitals and eight electrons. The active orbitals are described from the irreducible symmetry representation of the  $C_{2v}$  point group ( $a_1, b_1, b_2, a_2$ ) as (4, 2, 2, 0). The SA-CASSCF wave function was subsequently used in a MRCI calculation, the results of which are referred to as SA-MRCI. A series of correlation consistent basis sets<sup>70–72</sup> were used for the alkali metal in conjunction with singly augmented correlation consistent basis sets<sup>70,73,74</sup> for the halide. For a given “cardinal index,” X, the basis used was cc-pVXZ/aug-cc-pVXZ for the alkali metal/halide, respectively. The cardinal indices used were “T, Q, 5” in common notation or “3, 4, 5” in the numerical notation used in CBS extrapolation methods. Within the text, the shorthand notation aXZ will be used to refer to the split basis. Inclusion of augmentation functions on the alkali metal was examined and found to play a negligible role in the relevant atomic properties of the metal. For a given dimer and field, a consistent set of internuclear separations were used with respect to cardinal index. A list of the exact internuclear separations

used for each dimer and field are provided in the supplementary material.<sup>38</sup> All calculations were performed with the MOLPRO 2000<sup>75</sup> software program.

## B. Complete basis limit extrapolation procedures

### 1. Direct extrapolation of properties

From the series of *ab initio* calculated surfaces, a series of properties, e.g., equilibrium separation ( $R_e$ ), disassociation energy ( $D_e$ ), etc., can be extrapolated to the CBS limit. Two common extrapolation forms are considered here: the mixed Gaussian/exponential form of Woon and Dunning<sup>43,44</sup> (CBS<sub>MIX</sub>) and the exponential form suggested by Feller<sup>39–41</sup> (CBS<sub>EXP</sub>).

In both of the CBS extrapolation procedures, the property of interest at a given basis-set level is modeled by a parametric form. The parameters, one of which corresponds to the property value at the CBS limit, are obtained by a nonlinear minimization procedure of a  $\chi^2$  function of the form

$$\chi^2(A^{\text{CBS}}, B^{\text{CBS}}, C^{\text{CBS}}) = \sum_{x=3}^5 (\tilde{A}(x; A^{\text{CBS}}, B^{\text{CBS}}, C^{\text{CBS}}) - A(x))^2, \quad (2)$$

where  $A(x)$  is the property calculated with the basis set characterized by the “cardinal index”<sup>76</sup>  $x$  (i.e.,  $x=3, 4, 5$  for basis sets aTZ, aQZ and a5Z, respectively), and  $\tilde{A}(x; A^{\text{CBS}}, B^{\text{CBS}}, C^{\text{CBS}})$  is the CBS model value for the same cardinal index. The parameters in the CBS model are generically denoted  $A^{\text{CBS}}$ ,  $B^{\text{CBS}}$ , and  $C^{\text{CBS}}$  (see the following for the specific CBS<sub>MIX</sub> and CBS<sub>EXP</sub> model forms), where  $A^{\text{CBS}}$  represents the property value at the CBS limit. In the case that the property of interest is the energy itself, it will have an explicit dependence on the internuclear separation  $r$ , i.e.,  $A^{\text{CBS}} = E^{\text{CBS}}(r)$ . A complete knowledge of  $E^{\text{CBS}}(r)$  forms a potential energy surface, from which other important properties can be derived such as the minimum energy internuclear distance ( $R_e$ ), binding energy well depth ( $D_e$ ). Hence, there are two ways one can estimate the values of such properties at the CBS limit: by direct CBS extrapolation via minimization of Eq. (2) with respect to the parameters  $A^{\text{CBS}}$ ,  $B^{\text{CBS}}$ , and  $C^{\text{CBS}}$  (the optimized value of  $A^{\text{CBS}}$  providing the CBS limit value), or by derivation from the CBS potential energy curve  $E^{\text{CBS}}(r)$ . To distinguish the CBS property values determined from these two procedures, the values of the latter (i.e., the value of the property from the CBS extrapolated surface) will henceforth be superscripted with an asterisk (e.g.,  $A^{\text{CBS}*}$ ).

The mixed Gaussian/exponential scheme used here, denoted CBS<sub>MIX</sub>, was first suggested by Woon and Dunning,<sup>43,44</sup> and has the form

$$\tilde{A}(x) = A^{\text{CBS}_{\text{MIX}}} + B^{\text{CBS}_{\text{MIX}}} e^{-(x-1)} + C^{\text{CBS}_{\text{MIX}}} e^{-(x-1)^2}, \quad (3)$$

where  $A^{\text{CBS}_{\text{MIX}}}$  is the CBS limit value estimated from the “CBS<sub>MIX</sub>” extrapolation scheme, and, as mentioned earlier, the index  $x$  corresponds to the cardinal index<sup>76</sup> of the basis.

This same property  $A$ , if derived from the CBS potential energy curve  $E^{\text{CBS}_{\text{MIX}}}(r)$ , is designated with an asterisk as  $A^{\text{CBS}_{\text{MIX}}*}$ .

The second type of CBS extrapolation procedure considered, CBS<sub>EXP</sub>, is the exponential form proposed by Feller,<sup>39–41</sup>

$$\tilde{A}(x) = A^{\text{CBS}_{\text{EXP}}} + B^{\text{CBS}_{\text{EXP}}} e^{-x C^{\text{CBS}_{\text{EXP}}}}. \quad (4)$$

As before,  $x$  is the “cardinal index” of the basis,  $A^{\text{CBS}_{\text{EXP}}}$  is the estimated CBS limit value for property  $A$ , and  $B^{\text{CBS}_{\text{EXP}}}$  and  $C^{\text{CBS}_{\text{EXP}}}$  are parameters determined through the optimization of Eq. (2).

### 2. Extrapolation of adiabatic surfaces from the diabatic representation

The two lowest adiabatic energies, molecular dipole moments, and transition dipole moments were calculated at each internuclear separation. The avoided crossing exhibited by these systems result in large changes in the qualitative and quantitative trends in the values of these properties near the crossing distance. The location of the crossing distance is extremely sensitive to basis quality, and direct CBS extrapolation of the adiabatic data is of questionable reliability in this region of the PES. A simple two-state model can be used to construct a set of diabatic states (see the following) that are stable and smooth, even in the region of the crossing distance, and can be used to construct an accurate, robust CBS extrapolation procedure for the systems in the present work.

Let the wave functions of the two lowest  $^1\Sigma^+$  states in the adiabatic representations be designated  $|\Psi_1^{\text{ad}}\rangle$  and  $|\Psi_2^{\text{ad}}\rangle$ , respectively. A set of two corresponding diabatic states,  $|\Psi_1^{\text{d}}\rangle$  and  $|\Psi_2^{\text{d}}\rangle$ , can be derived using a simple two state model. The adiabatic and diabatic states are related by a unitary transformation

$$|\Psi_i^{\text{d}}\rangle = \sum_{k=1}^2 |\Psi_k^{\text{ad}}\rangle U_{ki}^* \quad (5)$$

or more compactly

$$\Psi^{\text{d}} = \mathbf{U}^\dagger \cdot \Psi^{\text{ad}}, \quad (6)$$

where  $\Psi_i^{\text{ad}}$  and  $\Psi_i^{\text{d}}$  are  $2 \times 1$  column vectors of the adiabatic and diabatic wave functions, respectively, represented in the basis of the adiabatic wave functions, and  $\mathbf{U}$  is the unitary transformation that relates them. The procedure for determination of the unitary transformation matrix follows that suggested by Werner and Meyer,<sup>15</sup> and uses the physical interpretation that, in the case of an alkali halide dimer oriented along the  $z$  direction, the atomic and ionic diabatic states can be distinguished by their molecular dipole moments. The adiabatic dipole and Hamiltonian matrices,  $\mathbf{D}^{\text{ad}}$  and  $\mathbf{A}^{\text{ad}}$ , are defined as

$$(\mathbf{D}^{\text{ad}})_{ij} = \langle \Psi_i^{\text{ad}} | \hat{z} | \Psi_j^{\text{ad}} \rangle, \quad (7)$$

$$(\mathbf{H}^{\text{ad}})_{ij} = \langle \Psi_i^{\text{ad}} | \hat{H} | \Psi_j^{\text{ad}} \rangle = E_j^{\text{ad}} \delta_{ij}, \quad (8)$$

where  $\hat{z}$  is the dipole operator for the dimer system oriented in the  $z$  direction that results in a nondiagonal matrix (the

diagonal elements being the ground and excited state molecular dipole moments, and the off-diagonal elements being the transition dipole moment), and  $\hat{H}$  is the Hamiltonian operator that, in the basis of the adiabatic wave functions, results in a diagonal matrix of the adiabatic state energies. Under the assumptions of the diabatic model, the dipole matrix in the diabatic representation,  $\mathbf{D}^d$ , is diagonal, and the Hamiltonian matrix is no longer diagonal, but contains off-diagonal coupling matrix elements. The matrix defining the unitary transformation ( $\mathbf{U}$ ) that relates the adiabatic and diabatic states is constructed from the eigenvectors of the adiabatic dipole matrix<sup>15</sup> (i.e., the transformation that diagonalizes  $\mathbf{D}^d$ ). The diabatic representation (i.e., the diagonal dipole matrix and nondiagonal Hamiltonian matrix) is thus defined as

$$\mathbf{D}^d = \mathbf{U}^\dagger \cdot \mathbf{D}^{\text{ad}} \cdot \mathbf{U}, \quad (9)$$

$$\mathbf{H}^d = \mathbf{U}^\dagger \cdot \mathbf{H}^{\text{ad}} \cdot \mathbf{U}. \quad (10)$$

The adiabatic matrices  $\mathbf{D}^{\text{ad}}$  and  $\mathbf{H}^{\text{ad}}$  are available from the electronic structure calculations at each basis set level, and are used to generate the corresponding diabatic matrices  $\mathbf{D}^d$  and  $\mathbf{H}^d$  from Eqs. (9) and (10).

CBS extrapolation of the diabatic matrices  $\mathbf{D}^d$  and  $\mathbf{H}^d$  proceeds as described in Sec. II B 1, i.e., through minimization of the  $\chi^2$  merit function of Eq. (2). For clarity, each diabatic property (dipole moment and energy of each state, and diabatic coupling matrix element) at each internuclear separation was extrapolated independently. Upon CBS extrapolation of the properties in the diabatic representation ( $\mathbf{D}^d \rightarrow \mathbf{D}^{\text{d,CBS}}$  and  $\mathbf{H}^d \rightarrow \mathbf{H}^{\text{d,CBS}}$ ), the CBS-extrapolated properties of the adiabatic representation ( $\mathbf{D}^{\text{ad,CBS}}$  and  $\mathbf{H}^{\text{ad,CBS}}$ ) are obtained via the reverse transformation

$$\mathbf{D}^{\text{ad,CBS}} = \mathbf{U} \cdot \mathbf{D}^{\text{d,CBS}} \cdot \mathbf{U}^\dagger, \quad (11)$$

$$\mathbf{H}^{\text{ad,CBS}} = \mathbf{U} \cdot \mathbf{H}^{\text{d,CBS}} \cdot \mathbf{U}^\dagger, \quad (12)$$

where the unitary transformation matrix  $\mathbf{U}^\dagger$  results from diagonalization of the CBS-extrapolated diabatic Hamiltonian matrix  $\mathbf{H}^{\text{d,CBS}}$  (i.e.,  $\mathbf{U}^\dagger$  is constructed from the eigenvectors of  $\mathbf{H}^{\text{d,CBS}}$ ). The CBS extrapolated diabatic and adiabatic energies and dipoles (including the diabatic coupling matrix element and adiabatic transition dipoles) for each alkali halide and field strength are available as supplementary material.

In summary, the CBS-extrapolated adiabatic properties (i.e., the adiabatic matrices  $\mathbf{D}^{\text{ad,CBS}}$  and  $\mathbf{H}^{\text{ad,CBS}}$ ) for each internuclear separation were obtained from the following procedure:

- (1) determine, at each basis set level, the diabatic matrices  $\mathbf{D}^d$  and  $\mathbf{H}^d$  from diagonalization of  $\mathbf{D}^{\text{ad}}$  and use of Eqs. (9) and (10);
- (2) perform direct CBS extrapolation of the diabatic matrices via minimization of the  $\chi^2$  merit function of Eq. (2) to obtain the CBS-extrapolated diabatic matrices  $\mathbf{D}^{\text{d,CBS}}$  and  $\mathbf{H}^{\text{d,CBS}}$ ;
- (3) determine the CBS-extrapolated adiabatic matrices  $\mathbf{D}^{\text{ad,CBS}}$  and  $\mathbf{H}^{\text{ad,CBS}}$  from diagonalization of  $\mathbf{H}^{\text{d,CBS}}$  and use of Eqs. (11) and (12).

This procedure was found to be reliable and resulted in a robust, convergent set of CBS-extrapolated property values.

### III. RESULTS AND DISCUSSION

#### A. Basis set convergence

The following describes the basis set convergence of molecular and ionic properties, and of the adiabatic potential energy and dipole surfaces in the presence and absence of applied fields.

#### 1. Convergence of properties with respect to basis set

Tables I–IV compare properties calculated at aTZ, aQZ, and a5Z basis set levels and calculated with several CBS extrapolation forms (“MIX” and “EXP”) and procedures (direct and indirect “\*\*”). The properties considered are the zero-crossing distance along the ground state repulsive wall ( $\sigma$ ), equilibrium separation ( $R_e$ ), dissociation energy ( $D_e$ ), ground state dipole moment expectation value evaluated at the equilibrium separation ( $\mu_{\text{eq}}$ ), crossing distance (defined as the distance at which the two diabatic energies are equal) ( $R_c$ ), diabatic coupling constant at the crossing distance ( $H_{12}$ ), and the “model” value of the crossing distance ( $\tilde{R}_c$ ) based on the asymptotic energy difference between the two electronic states at infinite separation in the absence of applied fields. The asymptotic limit of the energy difference ( $\Delta E_\infty$ ) was found by fitting the tail of the “atomic” and “ionic” diabatic energies (without applied electric fields) to  $r^{-6}$  and  $r^{-1}$  functions, respectively.  $\tilde{R}_c$  is related to  $\Delta E_\infty$  by

$$\tilde{R}_c = \frac{2}{\Delta E_\infty \pm \sqrt{\Delta E_\infty^2 - 4F}}. \quad (13)$$

$\tilde{R}_c$  is determined solely from the asymptotic energy difference and is thus useful for comparison against  $R_c$  to address the observations of Werner and Meyer<sup>15</sup> regarding the close relationship between the energy gap and observed crossing distance.

Most properties exhibit monotonic behavior with increasing basis set; however, there are some notable exceptions. Almost all of the examples of nonmonotonic behavior occur in the presence of applied fields. The most prominent example is with LiF where almost all of the “equilibrium” properties, i.e., those associated with the minimum on the PES, show nonmonotonic convergence with basis set (the exception being  $D_e$  at  $-0.0005$  a.u. field). Other less prominent examples occur with the  $\mu_{\text{eq}}$  and  $R_c$  values for LiCl with negative applied field. The only significant example of nonmonotonic behavior of properties that occurs at zero applied field is the  $\sigma$  values for NaF (2.653, 2.677, and 2.656 bohr at the aTZ, aQZ, and a5Z basis set levels, respectively).

Examination of the variation of the property values with basis set (independent of whether that variation is monotonic or not) reveals certain trends. The LiCl and NaCl systems appear to be particularly systematic in the range of variation or property values with respect to basis set, regardless of applied field. The geometrical properties  $\sigma$  and  $R_{\text{eq}}$  show relatively small variation with basis set, with the  $R_{\text{eq}}$  values

TABLE I. SA-MRCI basis set convergence properties of LiF.

| Field (a.u.) | Basis <sup>a</sup>   | $\sigma$ (bohr) | $R_{\text{eq}}$ (bohr) | $D_e$ ( $mE_h$ ) | $\mu_{\text{eq}}$ (a.u.) | $R_c$ (bohr) | $\tilde{R}_c$ (bohr) | $H_{12}$ ( $mE_h$ ) |
|--------------|----------------------|-----------------|------------------------|------------------|--------------------------|--------------|----------------------|---------------------|
| -0.0005      | T                    | 2.016           | 2.891                  | 211.04           | 2.459                    | 12.11        | 12.09                | 1.4035              |
|              | Q                    | 2.000           | 2.880                  | 214.99           | 2.453                    | 12.39        | 12.37                | 1.1983              |
|              | 5                    | 2.156           | 2.965                  | 216.54           | 2.529                    | 12.48        | 12.45                | 1.1442              |
|              | CBS <sub>MIX</sub>   | 2.117           | 3.015                  | 217.42           | 2.574                    | 12.53        | 12.50                | 1.1129              |
|              | CBS <sub>MIX</sub> * | <b>2.012</b>    | <b>2.967</b>           | <b>216.87</b>    | <b>2.530</b>             | <b>12.53</b> | <b>12.51</b>         | <b>1.1137</b>       |
|              | CBS <sub>EXP</sub>   | 2.117           | 2.958                  | 217.31           | 2.837                    | 12.52        | 12.48                | 1.1248              |
|              | CBS <sub>EXP</sub> * | <b>2.001</b>    | <b>2.971</b>           | <b>217.07</b>    | <b>2.551</b>             | <b>12.52</b> | <b>12.48</b>         | <b>1.1227</b>       |
| 0.0000       | T                    | 2.012           | 2.895                  | 212.65           | 2.468                    | 13.04        | 13.04                | 0.8983              |
|              | Q                    | 2.000           | 2.890                  | 216.79           | 2.455                    | 13.41        | 13.40                | 0.7364              |
|              | 5                    | 1.998           | 2.890                  | 217.46           | 2.455                    | 13.51        | 13.50                | 0.6951              |
|              | CBS <sub>MIX</sub>   | 1.997           | 2.890                  | 217.84           | 2.455                    | 13.57        | 13.56                | 0.6713              |
|              | CBS <sub>MIX</sub> * | <b>1.997</b>    | <b>2.890</b>           | <b>217.84</b>    | <b>2.455</b>             | <b>13.57</b> | <b>13.57</b>         | <b>0.6718</b>       |
|              | CBS <sub>EXP</sub>   | 1.998           | 2.890                  | 217.59           | 2.455                    | 13.56        | 13.54                | 0.6810              |
|              | CBS <sub>EXP</sub> * | <b>2.003</b>    | <b>2.890</b>           | <b>217.19</b>    | <b>2.455</b>             | <b>13.55</b> | <b>13.54</b>         | <b>0.6807</b>       |
|              | Expt. <sup>b</sup>   | NA              | 2.956                  | 219              | 2.488                    | NA           | 13.67                | NA                  |
| 0.0005       | T                    | 2.006           | 2.889                  | 214.08           | 2.463                    | 14.37        | 14.39                | 0.4674              |
|              | Q                    | 2.116           | 2.973                  | 218.67           | 2.542                    | 14.86        | 14.88                | 0.3578              |
|              | 5                    | 1.990           | 2.879                  | 218.06           | 2.459                    | 15.01        | 15.02                | 0.3308              |
|              | CBS <sub>MIX</sub>   | 1.918           | 2.823                  | 217.88           | 15.11                    | 2.409        | 15.09                | 0.3153              |
|              | CBS <sub>MIX</sub> * | <b>2.001</b>    | <b>2.877</b>           | <b>218.34</b>    | <b>2.457</b>             | <b>15.09</b> | <b>15.12</b>         | <b>0.3157</b>       |
|              | CBS <sub>EXP</sub>   | 1.990           | 2.879                  | 218.47           | 2.459                    | 15.09        | 15.08                | 0.3220              |
|              | CBS <sub>EXP</sub> * | <b>2.001</b>    | <b>2.876</b>           | <b>218.48</b>    | <b>2.456</b>             | <b>15.06</b> | <b>15.08</b>         | <b>0.3212</b>       |

<sup>a</sup>The basis is aug-cc-pVXZ for the halide and cc-pVXZ for the alkali atoms, where X is as given.

<sup>b</sup>Experimental values taken from Refs. 78 and 79.

more tightly converged. With the exception of LiF, the values of  $\sigma$  and  $R_{\text{eq}}$  at different basis sets span a range of approximately 0.02 and 0.01 bohr, respectively. For LiF, the variation of  $\sigma$  and  $R_{\text{eq}}$  values in the presence of applied field

shows significantly larger variation (approximately 0.14 and 0.09 bohr, respectively). Basis set variation of  $D_e$  and  $\mu_{\text{eq}}$  values span a range of approximately 5  $mE_h$  and 0.02 a.u., respectively. Values of  $R_c$  show larger basis set variation

TABLE II. SA-MRCI basis set convergence properties of LiCl.

| Field (a.u.) | Basis <sup>a</sup>   | $\sigma$ (bohr) | $R_{\text{eq}}$ (bohr) | $D_e$ ( $mE_h$ ) | $\mu_{\text{eq}}$ (a.u.) | $R_c$ (bohr) | $\tilde{R}_c$ (bohr) | $H_{12}$ ( $mE_h$ ) |
|--------------|----------------------|-----------------|------------------------|------------------|--------------------------|--------------|----------------------|---------------------|
| -0.0005      | T                    | 2.663           | 3.808                  | 168.84           | 2.818                    | 12.65        | 12.56                | 1.8596              |
|              | Q                    | 2.647           | 3.802                  | 172.72           | 2.819                    | 13.13        | 13.05                | 1.4317              |
|              | 5                    | 2.641           | 3.799                  | 173.89           | 2.816                    | 13.26        | 13.18                | 1.3333              |
|              | CBS <sub>MIX</sub>   | 2.638           | 3.797                  | 174.57           | 2.815                    | 13.34        | 13.25                | 1.2766              |
|              | CBS <sub>MIX</sub> * | <b>2.638</b>    | <b>3.797</b>           | <b>174.57</b>    | <b>2.815</b>             | <b>13.35</b> | <b>13.25</b>         | <b>1.2751</b>       |
|              | CBS <sub>EXP</sub>   | 2.641           | 3.799                  | 174.40           | 2.816                    | 13.34        | 13.22                | 1.3039              |
|              | CBS <sub>EXP</sub> * | <b>2.638</b>    | <b>3.797</b>           | <b>174.40</b>    | <b>2.815</b>             | <b>13.31</b> | <b>13.22</b>         | <b>1.3019</b>       |
| 0.0000       | T                    | 2.660           | 3.814                  | 170.30           | 2.836                    | 13.69        | 13.63                | 1.1294              |
|              | Q                    | 2.645           | 3.808                  | 174.18           | 2.836                    | 14.32        | 14.26                | 0.8023              |
|              | 5                    | 2.638           | 3.805                  | 175.35           | 2.833                    | 14.48        | 14.43                | 0.7329              |
|              | CBS <sub>MIX</sub>   | 2.635           | 3.803                  | 176.03           | 2.831                    | 14.58        | 14.53                | 0.6933              |
|              | CBS <sub>MIX</sub> * | <b>2.635</b>    | <b>3.803</b>           | <b>176.03</b>    | <b>2.832</b>             | <b>14.59</b> | <b>14.53</b>         | <b>0.6933</b>       |
|              | CBS <sub>EXP</sub>   | 2.638           | 3.804                  | 175.84           | 2.831                    | 14.61        | 14.49                | 0.7142              |
|              | CBS <sub>EXP</sub> * | <b>2.634</b>    | <b>3.802</b>           | <b>175.85</b>    | <b>2.832</b>             | <b>14.54</b> | <b>14.49</b>         | <b>0.7117</b>       |
|              | Expt. <sup>b</sup>   | NA              | 3.819                  | 179              | 2.804                    | NA           | 15.30                | NA                  |
| 0.0005       | T                    | 2.658           | 3.818                  | 171.71           | 2.852                    | 15.23        | 15.21                | 0.5284              |
|              | Q                    | 2.642           | 3.812                  | 175.59           | 2.852                    | 16.12        | 16.11                | 0.3257              |
|              | 5                    | 2.636           | 3.809                  | 176.75           | 2.849                    | 16.37        | 16.36                | 0.2834              |
|              | CBS <sub>MIX</sub>   | 2.633           | 3.807                  | 177.43           | 2.848                    | 16.52        | 16.51                | 0.2591              |
|              | CBS <sub>MIX</sub> * | <b>2.632</b>    | <b>3.807</b>           | <b>177.43</b>    | <b>2.848</b>             | <b>16.52</b> | <b>16.51</b>         | <b>0.2605</b>       |
|              | CBS <sub>EXP</sub>   | 2.636           | 3.805                  | 177.11           | 2.849                    | 16.63        | 16.45                | 0.2722              |
|              | CBS <sub>EXP</sub> * | <b>2.632</b>    | <b>3.806</b>           | <b>177.26</b>    | <b>2.848</b>             | <b>16.45</b> | <b>16.45</b>         | <b>0.2708</b>       |

<sup>a</sup>The basis is aug-cc-pVXZ for the halide and cc-pVXZ for the alkali atoms, where X is as given.

<sup>b</sup>Experimental values taken from Refs. 78 and 79.

TABLE III. SA-MRCI basis set convergence properties of NaF.

| Field (a.u.)       | Basis <sup>a</sup>   | $\sigma$ (bohr) | $R_{\text{eq}}$ (bohr) | $D_e$ ( $mE_h$ ) | $\mu_{\text{eq}}$ (a.u.) | $R_c$ (bohr) | $\bar{R}_c$ (bohr) | $H_{12}$ ( $mE_h$ ) |
|--------------------|----------------------|-----------------|------------------------|------------------|--------------------------|--------------|--------------------|---------------------|
| -0.0005            | T                    | 2.662           | 3.631                  | 174.98           | 3.290                    | 14.37        | 14.37              | 0.5271              |
|                    | Q                    | 2.651           | 3.631                  | 177.60           | 3.289                    | 14.77        | 14.75              | 0.4242              |
|                    | 5                    | 2.640           | 3.629                  | 179.16           | 3.280                    | 14.89        | 14.87              | 0.3977              |
|                    | CBS <sub>MIX</sub>   | 2.634           | 3.628                  | 180.04           | 3.275                    | 14.96        | 14.94              | 0.3824              |
|                    | CBS <sub>MIX</sub> * | <b>2.640</b>    | <b>3.628</b>           | <b>180.09</b>    | <b>3.274</b>             | <b>14.97</b> | <b>14.94</b>       | <b>0.3825</b>       |
|                    | CBS <sub>EXP</sub>   | 2.640           | 3.627                  | 179.38           | 3.280                    | 14.95        | 14.93              | 0.3885              |
|                    | CBS <sub>EXP</sub> * | <b>2.632</b>    | <b>3.629</b>           | <b>181.35</b>    | <b>3.280</b>             | <b>14.94</b> | <b>14.92</b>       | <b>0.3879</b>       |
| 0.0000             | T                    | 2.653           | 3.643                  | 177.20           | 3.307                    | 16.00        | 16.03              | 0.2392              |
|                    | Q                    | 2.677           | 3.628                  | 179.19           | 3.290                    | 16.57        | 16.55              | 0.1773              |
|                    | 5                    | 2.656           | 3.627                  | 180.76           | 3.283                    | 16.73        | 16.72              | 0.1626              |
|                    | CBS <sub>MIX</sub>   | 2.644           | 3.626                  | 181.64           | 3.279                    | 16.82        | 16.82              | 0.1541              |
|                    | CBS <sub>MIX</sub> * | <b>2.648</b>    | <b>3.626</b>           | <b>181.70</b>    | <b>3.279</b>             | <b>16.83</b> | <b>16.82</b>       | <b>0.1542</b>       |
|                    | CBS <sub>EXP</sub>   | 2.655           | 3.627                  | 181.15           | 3.278                    | 16.83        | 16.80              | 0.1579              |
|                    | CBS <sub>EXP</sub> * | <b>2.634</b>    | <b>3.630</b>           | <b>183.02</b>    | <b>3.159</b>             | <b>16.79</b> | <b>16.79</b>       | <b>0.1570</b>       |
| Expt. <sup>b</sup> | NA                   | 3.640           | 197                    | 3.208            | NA                       | 15.66        | NA                 |                     |
| 0.0005             | T                    | 2.653           | 3.644                  | 177.62           | 3.308                    | 16.00        | 18.89              | 0.0551              |
|                    | Q                    | 2.650           | 3.637                  | 181.19           | 3.304                    | 19.77        | 19.79              | 0.0358              |
|                    | 5                    | 2.640           | 3.635                  | 182.68           | 3.294                    | 20.07        | 20.10              | 0.0306              |
|                    | CBS <sub>MIX</sub>   | 2.635           | 3.634                  | 183.53           | 3.289                    | 20.84        | 20.28              | 0.0276              |
|                    | CBS <sub>MIX</sub> * | <b>2.638</b>    | <b>3.633</b>           | <b>183.57</b>    | <b>3.289</b>             | <b>20.22</b> | <b>20.28</b>       | <b>0.0280</b>       |
|                    | CBS <sub>EXP</sub>   | 2.640           | 3.634                  | 183.37           | 3.294                    | 20.07        | 20.24              | 0.0287              |
|                    | CBS <sub>EXP</sub> * | <b>2.631</b>    | <b>3.633</b>           | <b>184.31</b>    | <b>3.289</b>             | <b>19.44</b> | <b>20.22</b>       | <b>0.0166</b>       |

<sup>a</sup>The basis is aug-cc-pVXZ for the halide and cc-pVXZ for the alkali atoms, where X is as given.

<sup>b</sup>Experimental values taken from Refs. 78 and 79.

with applied field along the dipole axis (i.e., as the ionic states become stabilized and  $R_c$  itself becomes larger), and the diabatic coupling constant at the crossing distance ( $H_{12}$ ) show correspondingly lower variation. In the case of NaF, the  $R_c$  values for 0.0005 a.u. applied field range from 14 to 20 bohr going from aTZ–a5Z basis sets.

Section III B 2 continues a discussion of Tables I–IV as it relates to the CBS extrapolation procedures.

## 2. Convergence of adiabatic surfaces

To illustrate the convergence trends of the potential energy and dipole surfaces with respect to basis set and CBS

TABLE IV. SA-MRCI basis set convergence properties of NaCl.

| Field (a.u.)       | Basis <sup>a</sup>   | $\sigma$ (bohr) | $R_{\text{eq}}$ (bohr) | $D_e$ ( $mE_h$ ) | $\mu_{\text{eq}}$ (a.u.) | $R_c$ (bohr) | $\bar{R}_c$ (bohr) | $H_{12}$ ( $mE_h$ ) |
|--------------------|----------------------|-----------------|------------------------|------------------|--------------------------|--------------|--------------------|---------------------|
| -0.0005            | T                    | 3.262           | 4.468                  | 145.35           | 3.621                    | 15.08        | 15.01              | 0.6471              |
|                    | Q                    | 3.247           | 4.462                  | 149.19           | 3.622                    | 15.76        | 15.70              | 0.4482              |
|                    | 5                    | 3.242           | 4.457                  | 150.57           | 3.614                    | 15.94        | 15.88              | 0.4053              |
|                    | CBS <sub>MIX</sub>   | 3.239           | 4.454                  | 151.36           | 3.610                    | 16.05        | 15.99              | 0.4073              |
|                    | CBS <sub>MIX</sub> * | <b>3.237</b>    | <b>4.454</b>           | <b>151.37</b>    | <b>3.610</b>             | <b>16.05</b> | <b>15.99</b>       | <b>0.3818</b>       |
|                    | CBS <sub>EXP</sub>   | 3.239           | 4.457                  | 151.24           | 3.614                    | 16.10        | 15.95              | 0.3934              |
|                    | CBS <sub>EXP</sub> * | <b>3.235</b>    | <b>4.454</b>           | <b>151.30</b>    | <b>3.579</b>             | <b>16.01</b> | <b>15.95</b>       | <b>0.3918</b>       |
| 0.0000             | T                    | 3.258           | 4.474                  | 147.21           | 3.641                    | 16.95        | 16.91              | 0.2597              |
|                    | Q                    | 3.243           | 4.467                  | 151.05           | 3.641                    | 17.94        | 17.90              | 0.1531              |
|                    | 5                    | 3.238           | 4.462                  | 152.42           | 3.633                    | 18.21        | 18.17              | 0.1318              |
|                    | CBS <sub>MIX</sub>   | 3.235           | 4.460                  | 153.21           | 3.629                    | 18.37        | 18.33              | 0.1196              |
|                    | CBS <sub>MIX</sub> * | <b>3.234</b>    | <b>4.460</b>           | <b>153.21</b>    | <b>3.629</b>             | <b>18.37</b> | <b>18.33</b>       | <b>0.1209</b>       |
|                    | CBS <sub>EXP</sub>   | 3.238           | 4.462                  | 153.08           | 3.633                    | 18.53        | 18.27              | 0.1265              |
|                    | CBS <sub>EXP</sub> * | <b>3.232</b>    | <b>4.458</b>           | <b>153.15</b>    | <b>3.634</b>             | <b>18.31</b> | <b>18.27</b>       | <b>0.1250</b>       |
| Expt. <sup>b</sup> | NA                   | 4.462           | 156                    | 3.587            | NA                       | 17.83        | NA                 |                     |
| 0.0005             | T                    | 3.255           | 4.477                  | 149.01           | 3.659                    | 20.44        | 20.44              | 0.0445              |
|                    | Q                    | 3.240           | 4.471                  | 152.85           | 3.659                    | 22.33        | 22.38              | 0.0165              |
|                    | 5                    | 3.235           | 4.466                  | 154.21           | 3.652                    | 22.91        | 22.96              | 0.0120              |
|                    | CBS <sub>MIX</sub>   | 3.232           | 4.464                  | 155.00           | 3.647                    | 23.25        | 23.31              | 0.0095              |
|                    | CBS <sub>MIX</sub> * | <b>3.231</b>    | <b>4.464</b>           | <b>155.00</b>    | <b>3.647</b>             | <b>23.26</b> | <b>23.31</b>       | <b>0.0099</b>       |
|                    | CBS <sub>EXP</sub>   | 3.233           | 4.457                  | 154.90           | 3.651                    | 24.19        | 23.18              | 0.0112              |
|                    | CBS <sub>EXP</sub> * | <b>3.229</b>    | <b>4.463</b>           | <b>154.95</b>    | <b>3.632</b>             | <b>23.11</b> | <b>23.18</b>       | <b>0.0107</b>       |

<sup>a</sup>The basis is aug-cc-pVXZ for the halide and cc-pVXZ for the alkali atoms, where X is as given.

<sup>b</sup>Experimental values taken from Refs. 78 and 79.

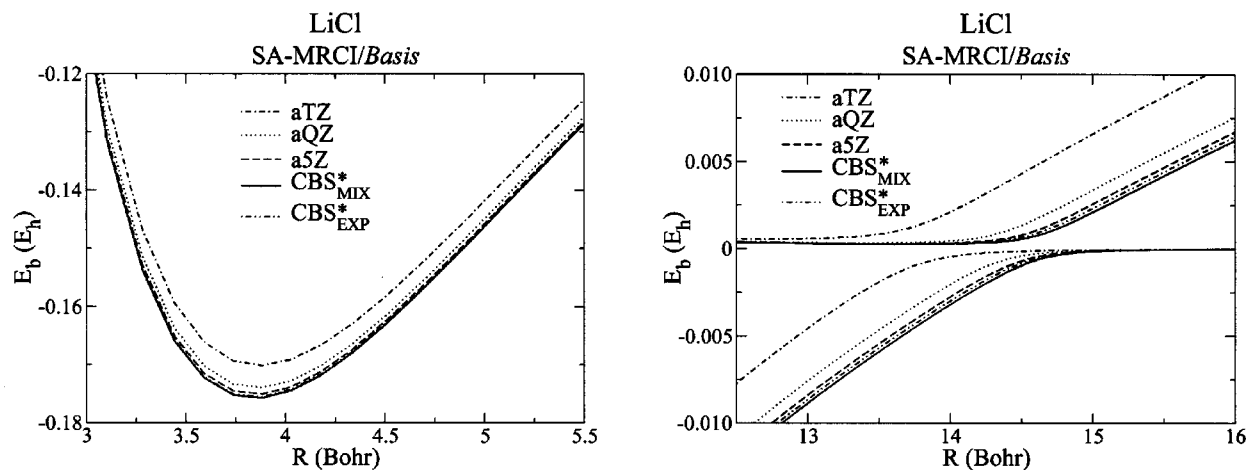


FIG. 1. Convergence behavior with respect to basis of the lowest adiabatic energy state of LiCl near the energy minimum (left panel) and the two lowest  $1\Sigma^+$  adiabatic energy states of LiCl near the avoided crossing (right panel) in the absence of applied electric fields.

extrapolation procedure, figures will focus on LiCl as an example (the other plots look qualitatively very similar). The tables present a complete set of results for all the properties.

Figure 1 illustrates the convergence of the adiabatic PESs of LiCl (without applied electric fields) with respect to basis set and form of CBS extrapolation method (MIX/EXP). The left panel shows the convergence of the ground state near the equilibrium distance and the right panel shows the two lowest  $1\Sigma^+$  adiabatic energies near the avoided crossing. The shorthand notation "aXZ" is used to denote the split cc-pVXZ/aug-cc-pVXZ basis discussed in Sec. II A. With increasing basis, the ground state energy near the equilibrium separation converges readily, i.e., the location of the equilibrium separation does not significantly change with respect to basis and the magnitude of the well depth increases with increasing basis. Similar convergence behavior is observed for the other alkali halide systems studied in this work (data not shown). This behavior suggests that a direct extrapolation of the adiabatic energies near the minimum may be reasonable. On the other hand, the location of the avoided crossing is sensitive to basis, causing qualitative differences in the behavior of the adiabatic energies calculated with different basis sets.

The two lowest  $1\Sigma^+$  adiabatic dipole moments of LiCl (without applied electric fields) near the crossing distance are shown in Fig. 2. From 13.7 to 14.5 bohr, the aTZ basis is beyond its crossing distance whereas the a5Z has yet to reach its crossing point. This results in large differences in the dipoles with respect to basis for any separation in this range and therefore makes direct extrapolation of the adiabatic data suspect. The CBS extrapolation procedure from the diabatic representation developed in this work overcomes these difficulties, and is the topic of the next section.

## B. CBS extrapolations

### 1. CBS extrapolation of adiabatic surfaces

Despite the sensitivity of the adiabatic surfaces and associated property values with basis set in the region of the avoided crossing, transformation into the diabatic representation results in a set of stable surfaces that are more ame-

nable to CBS extrapolation. The CBS extrapolation procedure in the diabatic representation described in Sec. II B 2 results in convergence of *both* the adiabatic energies at all internuclear separations and a converged location for the crossing point (Fig. 1).

Additionally, the dipole surfaces for the two lowest  $1\Sigma^+$  states are very well-behaved and follow closely the observed basis set trends (Fig. 2). A more sensitive test involves the examination of derivatives of the dipole moment surface in the region of the crossing point. A particularly useful quantity is the polarizability: the derivative of the dipole moment with respect to applied field. Figure 3 displays the polarizability surface as approximated from the CBS\*<sub>MIX</sub> extrapolated dipole surfaces with applied electric fields of LiCl over-set on the CBS\*<sub>MIX</sub> extrapolated dipole surface without applied electric fields. The crossing region is accompanied by a large change in the dipole moment and a large peak in the polarizability. This type of anomaly in the polarizability is intimately linked to the charge transfer, and represents an important phenomena to capture for models of biological

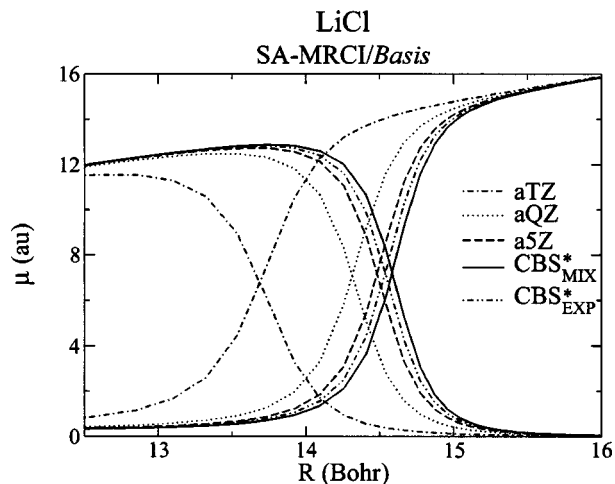


FIG. 2. Convergence behavior with respect to basis of the dipole moments corresponding to the two lowest  $1\Sigma^+$  adiabatic energy states of LiCl in the absence of applied electric fields.



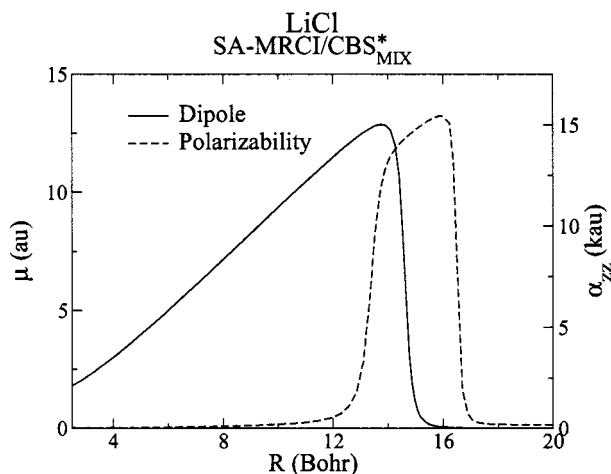


FIG. 3. The finite field approximation of the polarizability component along the internuclear axis of LiCl overset on the adiabatic ground state dipole moment in the absence of applied electric fields.  $-0.005$ ,  $0.0000$ , and  $0.0005$  a.u. field strengths were used in the finite differentiation of the dipole moment.

charge transfer events. This is an area that new-generation molecular simulation force fields have yet to overcome.

## 2. Comparison of CBS extrapolation procedures

Tables I–IV compare the convergence of properties with respect to basis and the results of the two extrapolation procedures discussed in Secs. II B 1 and II B 2. “CBS<sub>MIX</sub>” and “CBS<sub>EXP</sub>” refer to the direct extrapolation of properties appearing in the series aTZ, aQZ, and a5Z. “CBS<sub>MIX</sub>” and “CBS<sub>EXP</sub>” refer to the properties derived from the CBS extrapolated surfaces.

Comparison of the direct versus indirect CBS extrapolation procedure reveal property values that are very close. The indirect procedure shows slightly less variation in geometrical properties ( $\sigma$  and  $R_e$ ), but larger variation for the dissociation energy  $D_e$ . NaF exhibits particularly large variation for  $D_e$  between the CBS<sub>EXP</sub> and CBS<sub>EXP</sub> procedures (1.97, 1.87 and 0.94  $mE_h$  for  $-0.0005$ , 0, and 0.0005 a.u. applied fields, respectively), and between CBS<sub>MIX</sub> and CBS<sub>EXP</sub> methods. This in part arises from consistently larger  $D_e$  values for NaF predicted by CBS<sub>EXP</sub>. The predicted crossing distances are all in reasonable agreement between all the CBS forms and procedures, with the exception that there is considerably large variation between  $R_c$  values for NaCl predicted using the CBS<sub>EXP</sub> and CBS<sub>EXP</sub> procedures ( $R_c = 24.19$  and  $23.11$  for CBS<sub>EXP</sub> and CBS<sub>EXP</sub>, respectively). As with the observed basis set variation, variation within the CBS methods for  $R_c$  is larger with larger applied field causing stabilization of the ionic state. Overall the variation between CBS extrapolated values is considerably smaller than the corresponding basis set variation.

In most cases, properties converge with respect to basis smoothly; however, there are exceptions which make extrapolation of the properties suspect.<sup>42</sup> For example,  $\sigma$  of NaF without applied fields increases from 2.653 bohr (aTZ) to 2.677 bohr (aQZ) but then decreases to 2.656 bohr at the largest basis (a5Z). Interestingly, the two CBS<sub>MIX</sub> extrapola-

tion procedures agree to within 0.004 bohr to give values of 2.644 (CBS<sub>MIX</sub>) and 2.648 bohr (CBS<sub>MIX</sub>). The exponential extrapolation form agrees less (a difference of 0.021 bohr) and results in values of 2.655 (CBS<sub>EXP</sub>) and 2.634 bohr (CBS<sub>EXP</sub>).

An alternate source of skepticism arises from trends which are better described as divergent rather than convergent. For example,  $\mu_{eq}$  of LiCl for both 0.0005 and no applied field show no change upon increasing the basis from aTZ to aQZ but then slightly decrease with the a5Z basis. In both cases the extrapolation procedures and forms agree very well and may be attributed to the small magnitude of the “divergent” behavior.

The dipole moments discussed in the tables were determined as expectation values of the dipole operator. However, one can also approximate the value of  $\mu_{eq}$  through finite field differentiation of the energy evaluated at  $R_{eq}$  with respect to applied electric field. The  $\mu_{eq}$  values (in the absence of an applied field) obtained as dipole expectation values and as finite field ( $\pm 0.005$  a.u.) approximations using CBS<sub>MIX</sub> are: 2.455/2.584 (LiF), 2.832/2.815 (LiCl), 3.279/3.043 (NaF), and 3.629/3.611 (NaCl) a.u., respectively.

## C. The effect of electric field on crossing distance

Increase of the applied electric field from negative to positive stabilizes the ionic state and results in an increase in  $R_c$  and decrease in the value of  $H_{12}$ . The stabilization effects properties near the equilibrium separation as well. In most cases,  $R_e$ ,  $\mu_{eq}$ , and  $D_e$  increase and  $\sigma$  decreases with greater ion stabilization.

The  $R_c$  values for the alkali halide systems studied here follow the trend:

$$\text{LiF} < \text{LiCl} < \text{NaF} < \text{NaCl}.$$

This trend mimics the trend in  $\sigma$ ,  $R_{eq}$  and  $\mu_{eq}$  values, and is the reverse of trend in  $D_e$  values. The sensitivity of the crossing distances with respect to applied field follow the same trend as the  $R_c$  values.

The  $R_c$  value of LiCl is least affected by applied field and that of NaCl is most affected. The applied fields affect the  $R_c$  values in an asymmetric fashion: a larger affect is observed for fields that stabilize the ionic state. In the case of LiF, the average CBS extrapolated values for  $R_c$  are 12.53, 13.56, and 15.08 bohr; hence, a destabilizing  $-0.0005$  a.u. applied field causes a negative shift of the zero field  $R_c$  value of  $-1.03$  bohr, and a stabilizing 0.0005 a.u. field causes a positive shift of 1.52 bohr (roughly 50% difference in magnitude). This asymmetry becomes more exaggerated as the  $R_c$  values increase such that in the case of NaCl the average CBS extrapolated values for  $R_c$  are 16.05, 18.40, and 23.45 bohr, resulting in  $-2.34$  and 5.06 bohr negative and positive shifts with applied field (roughly 115% difference in magnitude).

## D. Comparison of CBS extrapolated crossing distances with previous work

The work of Sousa *et al.*<sup>14</sup> is important work to compare against. The authors developed a modified form of the Ritt-

TABLE V. Comparison of crossing distances.<sup>a</sup>

|    | Field   | F                   |                     |       |       | Cl                  |                     |       |       |
|----|---------|---------------------|---------------------|-------|-------|---------------------|---------------------|-------|-------|
|    |         | CBS* <sub>MIX</sub> | CBS* <sub>EXP</sub> | Sousa | Expt. | CBS* <sub>MIX</sub> | CBS* <sub>EXP</sub> | Sousa | Expt. |
| Li | -0.0005 | 12.53               | 12.52               | 12.0  | 12.59 | 13.35               | 13.31               | 13.7  | 13.83 |
|    | 0.0000  | 13.57               | 13.55               | 12.8  | 13.67 | 14.59               | 14.54               | 15.1  | 15.30 |
|    | 0.0005  | 15.09               | 15.06               | 13.9  | 15.26 | 16.52               | 16.45               | 17.0  | 17.69 |
| Na | -0.0005 | 14.97               | 14.94               | 13.8  | 14.10 | 16.05               | 16.01               | 15.8  | 15.65 |
|    | 0.0000  | 16.83               | 16.79               | 15.1  | 15.66 | 18.37               | 18.31               | 17.8  | 17.83 |
|    | 0.0005  | 20.22               | 19.44               | 17.1  | 18.27 | 23.26               | 23.11               | 22.0  | 22.24 |

<sup>a</sup>“CBS\*<sub>EXP</sub>” and “CBS\*<sub>MIX</sub>” refer to the crossing distance from the CBS extrapolated potential energy surfaces using the exponential and combined exponential/Gaussian forms respectively. “Sousa” refers to the MS-CASPT2 work of Ref. 14. “Exp” refers to the crossing distances as derived from the Rittner potential [Eq. (13)] using experimental (Ref. 79) ionization potentials (Li=0.198 14E<sub>h</sub> and Na=0.188 86E<sub>h</sub>) and electron affinities (F=0.124 99E<sub>h</sub> and Cl=0.132 77E<sub>h</sub>) in the calculation of  $\Delta E_{\infty}$ . All values are atomic units.

ner potential to account for applied electric fields and validate the MS-CASPT2 methodology which may be a preferred method for systems exhibiting discontinuities in the SA-CASSCF procedure.<sup>77</sup>

Table V compares the crossing distances of LiF, LiCl, NaF, and NaCl between those obtained from the CBS extrapolated surfaces, the work of Sousa *et al.*,<sup>14</sup> and the Rittner potential using experimental atomic ionization and electron affinities. In all cases, CBS\*<sub>MIX</sub> produces larger values of  $R_c$  than CBS\*<sub>EXP</sub> with the largest difference being 0.78 bohr (NaF, 0.0005 a.u. field). With the exception of LiCl, the CBS extrapolated surfaces result in values of  $R_c$  that are larger than those predicted by Sousa *et al.*<sup>14</sup> The difference between the CBS and Sousa results for  $R_c$  range from 0.2 (NaCl, -0.0005 a.u. field) to 3.1 (NaF, 0.0005 a.u. field) bohr. For LiF, the CBS extrapolated surfaces result in values of  $R_c$  that agree more closely with the Rittner potential than does the results of Sousa *et al.* for all field strengths. Alternatively, Sousa *et al.* agrees much more closely with the Rittner potential for all other data.

Comparison of  $R_c$  and  $\tilde{R}_c$  (the observed crossing distance and the crossing distance predicted solely on the asymptotic energy gap between the two lowest electronic states, respectively) in Tables I–IV shows a close agreement between the two quantities. This suggests the extent of agreement between the crossing distances predicted via the Rittner potential using experimental atomic properties and those observed on the CBS extrapolated PESs is strongly related to the extent of agreement between their asymptotic energy difference, as originally discussed by Werner and Meyer.<sup>15</sup>

#### IV. CONCLUSION

The weakly avoided crossing of alkali halide systems with and without applied electric fields was examined using full valence SA-MRCI methods in the complete basis set limit. Extrapolation of the diabatic representation and subsequent transformation into the adiabatic representation is shown to reproduce energy and dipole surfaces that obey the qualitative convergence behavior with respect to basis. The CBS extrapolated diabatic and adiabatic energies and dipoles are provided as supplementary material.<sup>38</sup>

Two extrapolation *procedures* for determination of properties in the CBS limit are compared. The two procedures are (1) the direct extrapolation of the property, and (2) determination of the property from CBS extrapolated potential and dipole surfaces. Properties such as equilibrium separation, dissociation energy, crossing distance, and diabatic coupling constant are shown to agree well between the two procedures for these systems.

Comparison of crossing distances obtained from the CBS extrapolated surfaces, the Rittner potential using experimental values of atomic properties, and the work of Sousa *et al.*<sup>14</sup> are made. The CBS extrapolated crossing distances agree very well with the Rittner potential for LiF and moderately well for LiCl, NaF, and NaCl. The set of CBS extrapolated SA-MRCI results, in both diabatic and adiabatic representations and provided over a wide range of internuclear separations, serve as an important set of benchmark calculations for the design of new-generation many-body force fields that strive to more rigorously model polarization and charge transfer events in large multi-scale problems.

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