An Effective Hamiltonian for an Electronically Excited Solute in a Polarisable Molecular Solvent

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Abstract

An effective Hamiltonian suitable for nonadiabatic molecular dynamics simulations is derived for the low-lying electronic states of a molecular ion interacting with an assembly of polarisable solvent molecules. The Hamiltonian includes both induction and low-frequency dispersion effects. It is based on a molecular treatment of the solvent, but is similar to effective Hamiltonians that treat the solvent as a dielectric continuum. The electronic structure of the solute is described in a space defined by the low-lying electronic states of the isolated molecule, and no assumptions are made about the form of the basis states. The effective Hamiltonian uses distributed multipoles and distributed transition multipoles, both of which may be obtained from ab initio calculations, to describe the charge distribution and polarisability of the molecular ion.

I. INTRODUCTION

Recent experimental studies of the photodissociation of molecular ions in clusters [1–5] and in solution [6–12] have highlighted a central issue in chemical dynamics: the influence of solvation on chemical bonding and reactivity. In these systems, as the solute ion dissociates the excess charge that was originally delocalised over the molecule localises onto one atom. This intramolecular charge flow is closely coupled to the dynamics of the surrounding medium, since an asymmetric solvent environment favours a compact atomic charge distribution over a diffuse molecular one. The magnitude and direction of the charge flow also depends sensitively on the nature of the solute electronic wavefunction: in states that are primarily bonding in character the component of the electronic polarisability parallel to the dissociating bond is positive, while in antibonding states it is *negative* [13, 14]. Thus when the ground-state solute ion is placed in an asymmetric solvent environment the charge flows in the direction of greater solvation, reducing the potential energy of the solute charge distribution, but when excited to an anti-bonding state the charge flows toward the less solvated atom [15, 16]. Moreover, a typical open-shell ion contains several near-degenerate valence states which can be transiently populated by nonadiabatic transitions during the course of the dissociation. Classical trajectory simulations of these complex dynamics require an accurate description of both the ground and the excited electronic states of the solvated ion at every time step. An accurate treatment of the excited states also requires that correlation between the solute electrons be included at a high level. Since full ab initio molecular dynamics is only feasible for the smallest clusters, a faster method must be devised. In this paper we derive an effective Hamiltonian for the solute electronic structure from an ab initio description of the isolated solute wavefunction and an electrostatic model of the solute-solvent interactions.

Previous simulations of photodissociation in these systems have been based upon empirical potential curves for the solute. In a pioneering study, Perera and Amar [17] observed that the bonding interaction in Br_2^- favours a delocalised charge distribution, $Br^{-1/2}$–$Br^{-1/2}$,

whereas solvation favours a localised charge distribution, Br^{-1}–Br, with all of the solvent molecules clustered around the anion. Perera and Amar modelled the transition from a delocalised to a localised charge distribution by assigning a partial charge to each bromine atom that varies with the Br–Br bond length: as the molecule dissociates, one atomic charge declines smoothly to zero and the full charge settles on the other atom. The same charge-switching model was adopted by Amar and Perera in studies of I_2^- in a carbon-dioxide cluster [18], and by Benjamin et $al.$ [19, 20] in studies of I_2^- and I_3^- in water and ethanol solutions. Unphysical features of this model are that the charge on each halogen atom is independent of the positions of the solvent molecules, and that the two bromine atoms in Br_2^- are not treated on an equal footing.

Subsequent models of photodissociation and recombination developed by our group [13, 14] and by Benjamin et $al.$ [9] removed these defects by using a Hückel-type model for the electronic structure of the solute. The Hückel Hamiltonian consists of an empirical set of potential surfaces for the isolated solute [21], together with a term describing the coulombic interaction of the solute with the solvent. The Hamiltonian allows for strong mixing of the near-degenerate states of the isolated solute, in contrast to the widely used electrostatic model of intermolecular forces [22], which assumes the electronic state of each molecule is only mildly perturbed by intermolecular interactions. These models allow the solute to be polarised by solvent, but the solvent itself is not polarisable.

A complete description of solvent-solute interactions must incorporate the electronic polarisability of the solvent molecules as well as their static charge distributions. This is critically important for solvents having no permanent moments at all, such as argon. The first theoretical studies to include solvent electronic polarisability were based on a dielectric continuum model of the solvent [23–29]. The most pertinent result of those studies is that the solute-solvent "dispersion" interaction, which arises from intermolecular electron correlation, must be included in order to obtain a qualitatively correct picture of solvation. In retrospect, this not surprising since the dispersion interaction is roughly proportional to both the solvent and the solute polarisabilities [30] and the near-degenerate states of the

solute are highly polarisable. Owing to the magnitude of the dispersion interaction, the usual perturbative treatment [31] cannot be applied. Thus, non-perturbative approaches had to be devised [24, 25, 27, 28]. Frequently an adiabatic separation can be made between the fast solvent polarisability and the relatively slow solute electrons [23–25], considerably simplifying the treatment of dispersion.

Early simulations were restricted to adiabatic dynamics on a single potential energy surface. More recently, nonadiabatic transitions were included explicitly by Batista and Coker, who studied the photodissociation of $I_2^- Ar_n$ using a model that includes the solvent electronic polarisability [32]. Their Hamiltonian [32–34] is based on the Diatomics in Ionic Systems model of Last and George [35], in which the semiempirical Diatomics in Molecules Hamiltonian is augmented by an operator representing the solvent polarisation energy produced by the solute charge. This treatment takes advantage of the adiabatic separation between solute and solvent electronic motion to obtain a relatively simple description of the solute-solvent dispersion interaction. The nonadiabatic transitions, which are essential for a consistent treatment of the photodissociation and subsequent recombination dynamics, were included using semiclassical surface-hopping methods [36–39]. Simulations using this model successfully reproduced the experimentally observed product distributions for the photodissociation of $I_2^- Ar_n$ clusters [32].

In recent publications [15, 16, 40] we have briefly outlined a different approach to this problem, one based on accurate ab initio solute wavefunctions rather than empirical models of the solute electronic structure. The ab initio approach offers a superior description of the solute charge distribution, and can be applied to more complex solute molecules for which an empirical parametrisation of the charge distribution is not feasible. It represents an extension of the conventional theory of long-range intermolecular forces [22] to account for the strong polarisation of the solute charge distribution and the exceptionally large solute-solvent dispersion interaction. The model successfully reproduces experimental product distributions [15, 16] and time-resolved photoelectron spectra [40].

The present paper is the first of two [41] devoted to explaining the details of our pro-

cedure. In this paper we derive *an effective Hamiltonian for the solute* that allows one to determine how the electronic states of the isolated solute are perturbed by the polarisable solvent. Our approach is explicitly molecular, but closely parallels treatments based on continuum dielectric models [23–25]. No assumptions are made about the form of the solute wavefunction; instead, our treatment is formulated using the distributed multipole analysis (DMA) [42–45], which is particularly well suited for dealing with charge densities that are obtained from ab initio calculations. An important feature of the effective Hamiltonian is its extensive use of the DMA for *transition* charge densities [45, 46]—matrix elements of the distributed multipole operators between two different molecular eigenstates. These transition densities allow the solute charge distribution to polarise in response to the external fields that act on it, and thus enable the model to describe solvent-induced charge localisation without adopting a localised representation for the solute basis functions. This is a significant practical advantage since ab initio electronic wavefunctions are often delocalised.

This paper is organised as follows. The effective Hamiltonian is derived in Section 2. We begin the derivation by reviewing the familiar expression for the induction energy of the solvent, and then show how this expression is modified when a solute having several low-lying excited states is incorporated into the solvent. In section 3, we discuss the methods used to evaluate the matrix elements of the effective Hamiltonian. Further discussion of the physical approximations made in deriving this Hamiltonian, and of its relationship to previous work, is included in section 4. Section 5 contains a brief summary.

II. DERIVATION OF THE EFFECTIVE HAMILTONIAN

In this section we derive an effective Hamiltonian for the interaction of the solute electrons with an arbitrary number of polarisable solvent molecules. First, we present an overview of the derivation.

Assuming the Born-Oppenheimer separation between the nuclear and electronic coordinates, we start by expressing the electronic Hamiltonian for the solute-solvent system as a

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function of the nuclear coordinates, using a distributed multipole (DM) expansion of the intermolecular coulombic interactions. Since this expansion neglects the repulsive interactions that arise when different molecular charge distributions overlap, we account for these interactions by adding a short-range term. The only assumption made about this short-range Hamiltonian is that it is unaffected by the solvent electronic polarisation. In other words, we assume that the polarisation of the solvent charge distribution is small enough so that the repulsive interactions due to charge overlap do not change substantially.

In Sec. II B we derive the induction energy of a polarisable solvent possessing permanent electrostatic moments using the DM notation. Although Stone has previously derived this expression using a perturbative approach [44], we present this alternative derivation because it forms a useful foundation for our work on solvent-solute interactions. We express the induction energy for the solvent as the expectation value of the Hamiltonian using a wavefunction that is a product of wavefunctions for each solvent molecule. Since this Hartree approximation neglects both the intermolecular electron correlation (dispersion) that arises from electronic motion and the exchange-repulsion interaction arising from short-range overlap, we account for these effects with the short-range terms added to the Hamiltonian. The induction energy is obtained by variationally optimising the induced multipoles on each solvent molecule, which is equivalent to optimising the solvent wavefunction.

We extend this treatment of the solvent electronic polarisation in Sec. II C to include interaction with the solute electrons. An effective Hamiltonian operator for the solute electrons is determined by variationally optimising the solvent-induced multipoles as before, but with an additional source term for the solute. This procedure assumes that the solvent electronic polarisation responds instantaneously to the fluctuations in the solute charge distribution that arise from motion of the solute electrons. This adiabatic separation has also been referred to as the Born-Oppenheimer limit for the solvent electronic polarisation [25], and its validity is discussed later in Sec. IV C. Essentially, it requires that the electronic states of the solute ion be much more closely spaced that those of the solvent, which is usually true for open-shell solute and closed-shell solvent molecules. Though the resulting

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effective Hamiltonian [Eq. (15)] operates only on the solute electrons, it depends on all of the nuclear coordinates and on the permanent moments and polarisabilities of the solvent molecules.

A. Hamiltonian for the Solute-Solvent System

The electrostatic potential arising from a molecular charge distribution may be expanded in a multipole series, the convergence of which may be greatly accelerated by using distributed multipoles instead of a single-centre expansion [42, 43, 45]. In particular, the distributed expansion converges for points that lie outside of the charge distribution but inside the molecular radius, where the single-centre expansion breaks down. In clusters and condensed phases molecules usually pack closely, so that accurate representation of the electrostatic interactions in this regime is essential.

In the DM expansion, several sites (usually atoms and bond centres) are chosen within each molecule, and then the multipoles for the entire molecule are partitioned into contributions from each of these sites. At each site the moments are expanded to a given order in real spherical tensor moments [47]. For example, the z component of the dipole moment at site i of molecule A is given by $Q_z^{A_i}$. The single-site multipole expansion can be recovered from the distributed-site expansion by use of multipole translation operators that shift the multipoles from all the distributed sites to a common site [42, 48–50].

The intermolecular electrostatic energy for non-overlapping charge distributions takes the form [44]

$$E^{\text{ele}} = \frac{1}{2} \sum_{A_i, B_j, t, u} Q_t^{A_i} T_{tu}^{A_i B_j} Q_u^{B_j} \tag{1}$$

where the sum runs over the sites and multipole orders on each pair of molecules in the system, and the factor of 1/2 compensates for double counting of the pairs. The elements of the interaction tensor T depend on the intermolecular distances and orientations. The element $T_{tu}^{A_i B_j}$ gives the coordinate dependence of the interaction between the multipole

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of order t on site i of molecule A and the multipole of order u on site j of molecule B. Although the tensor elements are rather complicated functions for all but the lowest order of multipoles, explicit expressions for them have been tabulated [45, 47, 51] and they may be computed efficiently even for high orders [48–50, 52]. Note that $T^{A_i A_j}$ *is always zero* because it is assumed that Coulomb interactions within a single molecule are accounted for in the intramolecular energy. In what follows we will usually suppress site indices and the order-component subscripts, writing the interaction between two molecules simply as $Q^A T^{AB} Q^B$.

The intermolecular components of the electronic Hamiltonian for the solute-solvent system may be expanded similarly in terms of distributed multipole *operators* [44, 45]. The classical multipoles used to obtain the interaction energy through Eq. (1) are simply the expectation values of these operators with respect to the molecular wavefunctions. The electronic Hamiltonian for the solute-solvent system then takes the form

$$
\begin{aligned}
\hat{\mathcal{H}} = \hat{h}^C + \sum_A \hat{H}^A \\
+ \frac{1}{2} \sum_{A,B} \hat{Q}^A T^{AB} \hat{Q}^B + \sum_A \hat{q}^C T^{CA} \hat{Q}^A \\
+ \hat{h}^{\mathrm{sr}}.
\end{aligned}
\tag{2}
$$

The indices A and B run over all molecules in the solvent, while C designates the solute ion. Upper and lower case operators act on the solvent and solute electrons, respectively. $\hat{H}$ and $\hat{h}$ are the electronic Hamiltonians of the isolated molecules, while $\hat{Q}$ and $\hat{q}$ are the DM operators of the solvent and solute. The operator $\hat{h}^{\mathrm{sr}}$ accounts for short-range interactions that arise from the overlap of charge distributions of neighbouring molecules. As mentioned above, we assume throughout the derivation that $\hat{h}^{\mathrm{sr}}$ is not affected by polarisation of the solvent and so is an operator only in the solute electronic space, although it does depend on the nuclear coordinates of both the solute and solvent.

B. Induction Energy of the Solvent

In order to demonstrate the variational optimisation of the multipoles induced in the polarisable solvent, we first consider the Hamiltonian for the solvent alone. This is given by the second and third terms in Eq. (2),

$$\begin{aligned} \hat{H}^{\mathrm{solv}} &= \sum_A \hat{H}^A + \frac{1}{2} \sum_{A,B} \hat{Q}^A T^{AB} \hat{Q}^B \\ &\equiv \hat{H}^{\mathrm{self}} + \hat{H}^{\mathrm{ele}} \end{aligned} \tag{3}$$

where we have dropped the short-range interactions for simplicity.

We assume that the wavefunction can be written as a Hartree product,

$$|\Psi^{\mathrm{solv}}\rangle = \prod_A |\overline{\psi}^A\rangle. \tag{4}$$

The Hartree approximation neglects intermolecular electron correlation, which gives rise to dispersion forces. However, except at short range dispersion interactions are often small compared to electrostatic interactions and thus we account for them empirically with our short-range interactions.

The ground state energy and wavefunction of the solvent in the Hartree approximation are determined by varying the single-molecule wavefunctions $|\overline{\psi}^A\rangle$ to minimise the expectation value of the solvent hamiltonian, $\langle \Psi^{\mathrm{solv}} | \hat{H}^{\mathrm{solv}} | \Psi^{\mathrm{solv}} \rangle$. This procedure is carried out in detail in Appendix A. In the present section we follow a more concise line of argument that closely parallels the classical derivation of the induction energy of an ensemble of polarisable bodies. The expectation value of $\hat{H}^{\mathrm{solv}}$ is expressed as a function of the permanent and induced moments on each molecule, and then variationally minimised with respect to the induced moments to obtain the induction energy.

The expectation values of each multipole operator can be written as the sum of a permanent and an induced moment,

$$\langle \overline{\psi}^A | \hat{Q}^A | \overline{\psi}^A \rangle \equiv Q^A + \delta Q^A \tag{5}$$

where the permanent moment Q^A is the expectation value of the operator with respect to the *isolated* molecular wavefunction, and δQ^A is the corresponding induced moment. The expectation value of $\hat{H}^{\mathrm{ele}}$ is then given by

$$
\begin{aligned}
E^{\mathrm{ele}}(\delta \mathbf{Q}) &= \frac{1}{2} \sum_{AB} (Q^A + \delta Q^A) T^{AB} (Q^B + \delta Q^B) \\
&= \frac{1}{2} (\mathbf{Q} + \delta \mathbf{Q}) \cdot \mathsf{T} \cdot (\mathbf{Q} + \delta \mathbf{Q})
\end{aligned}
\tag{6}
$$

where in the second line we have introduced a convenient matrix-vector notation. The components of the vector $\mathbf{Q}$ and the row and column indices of the matrix T run over all the solvent molecules.

In order to account fully for the electronic polarisation of the solvent molecules, we must add the work required to produce this polarisation. The "self-energy" of each solvent molecule, $\langle \overline{\psi}^A | \hat{H}^A | \overline{\psi}^A \rangle$, may be expanded in powers of the induced moments. The term linear in δQ^A must be zero, since otherwise the isolated molecule would possess induced moments. Assuming that the degree of polarisation is small, we truncate the expansion at second order to obtain:

$$
E^{\mathrm{self}}(\delta Q^A) = E^A + \frac{1}{2} \sum_{ijtu} \delta Q_t^{A_i} [\alpha^{-1}]_{tu}^{A_i A_j} \delta Q_u^{A_j}
\tag{7}
$$

where E^A is the internal energy of the isolated molecule A and $\alpha^{A_i A_j}$ is its polarisability tensor. We have written the self-energy expression in a form that allows for distributed polarisabilities relating multipoles of arbitrary order [44, 53]. If the induced moments are large, hyperpolarisability terms involving higher powers of the induced moments must also be included in the self-energy. Since E^A is just the internal energy of the isolated solvent molecule at the given intramolecular coordinates, it may be set to zero for a rigid molecule. For flexible molecules it is the potential function for the molecule's internal force field.

The total solvent energy is the sum of the electrostatic and self-energy contributions,

$$
E^{\mathrm{solv}}(\delta \mathbf{Q}) = E^{\mathrm{intra}} + \frac{1}{2} \delta \mathbf{Q} \cdot \boldsymbol{\alpha}^{-1} \cdot \delta \mathbf{Q} + \frac{1}{2} (\mathbf{Q} + \delta \mathbf{Q}) \cdot \mathsf{T} \cdot (\mathbf{Q} + \delta \mathbf{Q})
\tag{8}
$$

where we have extended the matrix notation to include a solvent polarisability matrix $\boldsymbol{\alpha}$. This matrix is block diagonal since it contains no elements connecting different molecules.

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E^{intra} is the total intramolecular energy of the isolated solvent molecules, which is just the sum of the internal energies E^A.

Since the energy expression is quadratic in the induced moments, minimising it leads to a linear response equation relating the induced and permanent moments in the solvent,

$$\delta \mathsf{Q} = - \left[\mathsf{T} + \boldsymbol{\alpha}^{-1} \right]^{-1} \cdot \mathsf{T} \cdot \mathsf{Q}$$
$$\equiv - \boldsymbol{\chi} \cdot \mathsf{T} \cdot \mathsf{Q}. \tag{9}$$

Here we have introduced the generalised electric susceptibility $\boldsymbol{\chi}$, which is a symmetric tensor. $\boldsymbol{\chi}$ describes the electronic polarisation response of the solvent to the generalised potential V given by

$$\mathsf{V} \equiv \mathsf{T} \cdot \mathsf{Q}. \tag{10}$$

. The generalised potential contains the electrostatic potential and its derivatives (field, field gradient, etc.) at every site in the solvent.

By eliminating the induced moments $\delta \mathsf{Q}$ from Eq. (8) via Eq. (9), we can write the minimised solvent energy in terms of the susceptibility and permanent moments,

$$E^{\text{solv}} = E^{\text{intra}} + \frac{1}{2} \mathsf{Q} \cdot \mathsf{T} \cdot \mathsf{Q} - \frac{1}{2} \mathsf{Q} \cdot \mathsf{T} \cdot \boldsymbol{\chi} \cdot \mathsf{T} \cdot \mathsf{Q}. \tag{11}$$

The second term in this equation is the electrostatic energy due to interactions between the permanent multipoles, while the third term is the induction energy arising from the induced moments. The solvent energy can also be written in terms of the generalised potential V in the compact form

$$E^{\text{solv}} = E^{\text{intra}} + \frac{1}{2} \mathsf{Q} \cdot \mathsf{V} - \frac{1}{2} \mathsf{V} \cdot \boldsymbol{\chi} \cdot \mathsf{V}. \tag{12}$$

From this expression it is clear that the electrostatic and induction energies written in the DM notation are simply a generalisation of the standard expressions for these quantities in terms of single-centre moments.

C. Effective Hamiltonian for the Solute-Solvent System

We now allow the solvent to polarise in response to the *solute*. To obtain an effective Hamiltonian that operates on the solute electrons, we average over the solvent electrons while allowing them to respond instantaneously to the solute electrons. The resulting expression for $\hat{h}^{\text{eff}}$ in terms of the induced solvent moments is very similar to Eq. (8),

$$\hat{h}^{\text{eff}}(\delta\mathbf{Q}) = E^{\text{intra}} + \hat{h}^C + \hat{h}^{\text{sr}}$$
$$+\frac{1}{2}\delta\mathbf{Q} \cdot \boldsymbol{\alpha}^{-1} \cdot \delta\mathbf{Q}$$
$$+\frac{1}{2}(\mathbf{Q} + \hat{\mathbf{q}} + \delta\mathbf{Q}) \cdot \mathsf{T} \cdot (\mathbf{Q} + \hat{\mathbf{q}} + \delta\mathbf{Q}) \tag{13}$$

where we have extended the rows and columns of the matrix T to include both solvent and solute. Note that the intramolecular term $\frac{1}{2}\hat{\mathbf{q}} \cdot \mathsf{T} \cdot \hat{\mathbf{q}}$ does not contribute to the Hamiltonian because all the intramolecular elements of T are zero, and that the vector $\mathbf{Q}$ has non-zero multipoles only at the solvent sites, while $\hat{\mathbf{q}}$ has non-zero multipoles only at the solute sites.

The induced moments on the solvent molecules are obtained by variational minimisation as before. Since the part of Eq. (13) that depends on $\delta\mathbf{Q}$ differs from Eq. (8) only by the addition of $\hat{\mathbf{q}}$ to the electrostatic term, it is not surprising that the induced moments are given by

$$\delta\mathbf{Q} = -\boldsymbol{\chi} \cdot \mathsf{T} \cdot (\mathbf{Q} + \hat{\mathbf{q}}) \tag{14}$$

which differs from the linear response of the solvent alone by the addition of the solute multipole operators as a source term. The induced solvent multipoles are now given by an operator in the solute space, reflecting the fact that the solvent electrons adjust instantaneously to the positions of the solute electrons. Equation (14) may be used to eliminate $\delta\mathbf{Q}$ from Eq. (13) giving the effective Hamiltonian for the solute-solvent system:

$$\hat{h}^{\text{eff}} = E^{\text{intra}} + \hat{h}^C + \hat{h}^{\text{sr}}$$
$$+\frac{1}{2}(\mathbf{Q} + \hat{\mathbf{q}}) \cdot \mathsf{T} \cdot (\mathbf{Q} + \hat{\mathbf{q}})$$
$$-\frac{1}{2}(\mathbf{Q} + \hat{\mathbf{q}}) \cdot \mathsf{T} \cdot \boldsymbol{\chi} \cdot \mathsf{T} \cdot (\mathbf{Q} + \hat{\mathbf{q}}). \tag{15}$$

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Introducing the generalised-potential operator arising from the solute, $\hat{v} = \mathsf{T} \cdot \hat{\mathsf{q}}$, this can be rewritten as

$$
\begin{aligned}
\hat{h}^{\text{eff}} = {} & E^{\text{intra}} + \hat{h}^C + \hat{h}^{\text{sr}} \\
& + \frac{1}{2} (\mathsf{Q} + \hat{\mathsf{q}}) \cdot (\mathsf{V} + \hat{\mathsf{v}}) \\
& - \frac{1}{2} (\mathsf{V} + \hat{\mathsf{v}}) \cdot \boldsymbol{\chi} \cdot (\mathsf{V} + \hat{\mathsf{v}})
\end{aligned}
\tag{16}
$$

Equations (15) and (16) express the Hamiltonian for the solute-solvent system in terms of operators $\hat{h}$, $\hat{q}$ and $\hat{v}$ that act only on the solute electrons. The Hamiltonian depends parametrically upon the nuclear coordinates of both solute and solvent. As we discuss in more detail later, the two-electron operator $\hat{\mathsf{v}} \cdot \boldsymbol{\chi} \cdot \hat{\mathsf{v}}$ has contributions from both induction and dispersion interactions. We now discuss how the effective Hamiltonian is evaluated by the introduction of a basis for the solute space and an electrostatic model for the solvent.

III. EVALUATION OF THE EFFECTIVE HAMILTONIAN

A. Solute Basis

The effective Hamiltonian, $\hat{h}^{eff}$, may be evaluated in any representation, its eigenvalues depending upon the space spanned by the solute basis but not upon the choice of basis functions for that space. A natural choice of basis is the set of eigenstates of the isolated solute, in which the diagonal elements of $\hat{h}^C$ are the potential energy surfaces of the isolated solute.

The diagonal elements of $\hat{h}^{\text{eff}}$ modify the isolated solute potential surfaces to take into account the interaction of each of these states with the solvent, while the off-diagonal elements allow the solute to polarise in response to the solvent. In practice it is necessary to truncate the space of solute electronic states when evaluating $\hat{h}^{\text{eff}}$. For open-shell ionic solutes it is often sufficient to include only the valence states, since these enable intramolecular charge-transfer and hence account for the majority of the polarisation response. Both bond-

ing and anti-bonding states must be included in order to correctly describe the molecular polarisability.

In our applications to solvated I_2^- [15,16,40] the lowest six electronic states were retained, comprising all states that correlate to I^- (^1S) + I (^2P). No information about higher electronic states is known either from experiment or from theory. [54] An additional complication in I_2^- is its large spin-orbit coupling, which leads to a transition from eigenstates that are predominantly Hund's case (a) in character at the equilibrium bond length to states that are case (c) at large bond distances [54]. Since each state in this open-shell system has a twofold spin degeneracy by Kramers' theorem, $\hat{h}^{\mathrm{eff}}$ is represented by a 12×12 matrix.

The eigenvalues of $\hat{h}^{\mathrm{eff}}$ are the multidimensional potential energy surfaces of the entire solute-solvent system. At each step of a molecular dynamics simulation $\hat{h}^{\mathrm{eff}}$ is evaluated and diagonalised to give the energies and forces required to propagate the trajectory to the next step.

B. Coulombic Interactions

Evaluation of $\hat{h}^{\mathrm{eff}}$ requires a set of permanent multipoles and polarisabilities for the solvent and evaluation of the solute DM operators. The electrostatic properties of the solvent can be obtained from a wide variety of sources [31, 45, 55, 56]. For a simple solvent such as argon, only the point polarisability is needed for a reasonably accurate representation. Higher order polarisabilities and hyperpolarisabilities have a negligible effect on the interaction energy, especially given the uncertainties in the short-range interactions. For CO_2, we have found that a five-site distributed charge model [57], combined with single-centre parallel and perpendicular polarisabilities, [55] provides an adequate description. Higher order DM [43] and distributed polarisabilities [53] from ab initio calculations also exist for CO_2, but it is not clear that these give a more accurate description of the intermolecular potential [58].

Parametrisation of the solute is more involved. The matrix elements of the solute DM

operators are evaluated directly from the solute basis functions. For I_2^- we found that a four-site DM expansion up to quadrupole order was sufficient. Although DM's are widely used to represent the charge distribution of a single electronic state, a key feature of our effective Hamiltonian is the use of distributed *transition* multipoles [45, 46]. These off-diagonal DM's are not widely available for ab initio wavefunctions, and we have obtained them by a minor modification of the interface between Stone's DMA package and the ab initio program MOLPRO [59]. Calculation of the DM operators adds a negligible cost to the ab initio calculations. When the calculations are performed on a grid of solute geometries—we used 50 points for I_2^-— interpolation can be used to evaluate both the DM matrix elements and the electronic energy at arbitrary solute geometries.

The evaluation of the two-electron operator in the solute induction-dispersion term, $\hat{v} \cdot \chi \cdot \hat{v}$, requires further elaboration. The one-electron DM matrix elements q_{ij} are obtained from the ab initio calculation as described above. By inserting the identity, $\sum_k |k\rangle\langle k|$, and restricting the sum to the basis states of the solute, we can write the matrix elements of the two-electron operator in terms of one-electron matrix elements,

$$\left(\hat{v} \cdot \chi \cdot \hat{v}\right)_{ij} = \sum_k^{n_{\mathrm{basis}}} v_{ik} \cdot \chi \cdot v_{kj}. \tag{17}$$

This approximation is consistent with allowing the solute to polarise and fluctuate only in the space defined by the solute basis functions.

Evaluation of the susceptibility tensor χ is usually the most computationally demanding step in constructing $\hat{h}^{\mathrm{eff}}$. When only a single source term is present, it may be efficient to evaluate the induced moments, $\delta Q = -\chi \cdot V$, using an iterative procedure. Because the source term in $\hat{h}^{\mathrm{eff}}$ is an operator, however, a different set of induced moments must be computed for each pair of basis states. In clusters, where the number of polarisable sites is relatively small, it is therefore more efficient to compute χ directly by inverting the matrix $[T + \alpha^{-1}]$. This matrix is positive definite until the onset of polarisation catastrophe, which occurs when the polarisable sites on different molecules are too closely spaced [60]. Cholesky decomposition [61] is well suited for the computation of χ because it is highly efficient and

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fails for matrices that are not positive definite, providing a warning that the linear response approximation is no longer valid.

C. Short-range Interactions

The short-range effective Hamiltonian may be split into two components,

$$\hat{h}^{\mathrm{sr}} = \hat{h}^{\mathrm{sr}}_{sS} + E_{SS} \tag{18}$$

where s and S denotes the solute and solvent respectively. The solvent-solvent interaction energy, E_{SS}, is assumed to be independent of the solvent wavefunction, and so is simply a function of the solvent nuclear coordinates. In most potential models used for liquid simulations, the short-range interactions are represented by pairwise atom-atom Lennard-Jones potentials, while the long-range electrostatic interactions are calculated using distributed charges to represent the overall charge distribution. Such models, augmented by the inclusion of solvent polarisability, are easily applied to our effective Hamiltonian. We have used atom-atom Lennard-Jones potentials to represent the short-range solvent interactions in our initial applications to argon and CO_2 solvents [15, 16, 40].

Determining the short-range solute-solvent interactions is somewhat more complicated. In general, these interactions will depend on the electronic state of the solute. Our general approach has been to adopt the simplest potential model for the short-range interactions that will fit the available data from experiments. For both of the solvents that we have studied so far, we have fit state-independent atom-atom Lennard-Jones parameters to reproduce the potentials of I and I^- interacting with a single solvent molecule as determined by high-resolution photoelectron spectroscopy [62, 63]. These parameters alone were sufficient for $I_2^-(CO_2)_n$, but we found it necessary to introduce an additional state-dependent term to reproduce the anisotropy of the I–Ar interaction, which depends on the orientation of the iodine quadrupole moment [15].

D. Computation of Model Potential Surfaces

The eigenstates of $\hat{h}^{\text{eff}}$ are obtained at each step in a molecular dynamics simulation by the following process:

(1) Obtain solute basis state energies and distributed multipole operators from splined data evaluated at the current value of the solute internal coordinates. The energies of the solute basis states form the diagonal matrix $\hat{h}^C$.

(2) Compute coulombic terms in the expression for the effective Hamiltonian, the last two terms of Eq. (15), from the distributed solute multipoles, the solvent charge distribution, and the solvent polarisabilities.

(3) Calculate the solvent intramolecular energy, E^{intra}.

(4) Calculate the short-range interactions, $\hat{h}^{\text{sr}}$.

(5) Diagonalise $\hat{h}^{\text{eff}}$ to get eigenvectors and energies for all states.

(6) If necessary, compute the forces on the current adiabatic state by calculating the derivatives of the effective Hamiltonian with respect to the nuclear coordinates $\mathbf{R}$ and using the Hellmann-Feynman theorem,

$$\mathbf{F} = -\nabla_{\mathbf{R}}\langle\psi|\hat{h}^{\text{eff}}|\psi\rangle = -\langle\psi|\nabla_{\mathbf{R}}\hat{h}^{\text{eff}}|\psi\rangle. \tag{19}$$

IV. DISCUSSION

A. Solvent-solute interaction energy

The electronic energy of the solute-solvent system is the expectation value of $\hat{h}^{\text{eff}}$ with respect to the wavefunction of the solute,

$$\begin{aligned}
E(\psi) = {} & E^{\text{intra}} + \langle\psi|\hat{h}^C|\psi\rangle + \langle\psi|\hat{h}^{\text{sr}}|\psi\rangle \\
& + \frac{1}{2}\mathbf{Q}\cdot\mathbf{V} + \frac{1}{2}\mathbf{Q}\cdot\langle\psi|\hat{\mathbf{v}}|\psi\rangle + \frac{1}{2}\langle\psi|\hat{\mathbf{q}}|\psi\rangle\cdot\mathbf{V} \\
& - \frac{1}{2}\mathbf{V}\cdot\boldsymbol{\chi}\cdot\mathbf{V} - \frac{1}{2}\langle\psi|\hat{\mathbf{v}}|\psi\rangle\cdot\boldsymbol{\chi}\cdot\mathbf{V} - \frac{1}{2}\mathbf{V}\cdot\boldsymbol{\chi}\cdot\langle\psi|\hat{\mathbf{v}}|\psi\rangle \\
& - \frac{1}{2}\langle\psi|\hat{\mathbf{v}}\hat{\mathbf{v}}|\psi\rangle\cdot\boldsymbol{\chi}
\end{aligned} \tag{20}$$

in which the last line involves the scalar product of the second rank tensors $\hat{v}\hat{v}$ and χ. The term $1/2\langle\hat{q}\rangle \cdot \langle\hat{v}\rangle$ has been discarded since all intramolecular coulombic terms are zero.

The self-energy $\langle\hat{h}^C\rangle$ of the solute is evaluated exactly, rather than in the usual harmonic approximation [Eq. (7)], because the higher-order terms are essential for the description of a highly polarisable molecule. All the terms in Eq. (20) containing either the solvent multipoles Q or the solvent potential V describe electrostatic and induction interactions. The last term contains both induction and dispersion interactions:

$$-\frac{1}{2}\langle\hat{v}^2\rangle \cdot \chi = -\frac{1}{2}\langle\hat{v}\rangle \cdot \chi \cdot \langle\hat{v}\rangle \qquad \text{induction}$$
$$-\frac{1}{2}[\langle\hat{v}^2\rangle - \langle\hat{v}\rangle^2] \cdot \chi \qquad \text{dispersion.} \qquad (21)$$

The induction term describes the interaction of the solvent polarisability with the *average* potential arising from the charge distribution of the solute, $\langle\hat{v}\rangle$. The dispersion term arises from the interaction of the solvent polarisability with the fluctuations about this average, $[\langle\hat{v}^2\rangle - \langle\hat{v}\rangle^2]$. These fluctuations are due to motion of the solute electrons and may be exceptionally large when two potential surfaces are nearly degenerate. This is readily seen for the case of H_2^+ stretched almost to bond dissociation, where the charge distribution fluctuates between $H^+\ldots H$ and $H\ldots H^+$, with a mean charge of $1/2$ on each atom. Large fluctuations may occur whenever two Lewis structures are brought into resonance by solvation effects. Omission of the fluctuations leads to spurious localisation of the excess solute charge on a single atom, [23] since the induction energy is greatest if all the charge is concentrated at a single point. Because of the large magnitude of the solute fluctuations, it is essential to include them to obtain qualitatively correct results [23–25, 29, 64, 65]. This is in contrast to the much smaller fluctuations arising from the solvent electrons and from the core electrons in the solute, which are usually absorbed in the empirical short-range Hamiltonian.

The dispersion term in the energy expression, Eq. (21), arises because the solvent electronic polarisation is assumed to respond instantaneously to fluctuations of the valence solute electrons. Only the solute valence electron fluctuations are included because of the restriction of the solute basis to include only valence excitations. If instead the timescales

for the electronic motion in the solute and solvent were comparable, it would be more appropriate to use a Hartree-product wavefunction [Eq. (4)] for the entire solute-solvent system. The dispersion term would then be absent from the energy expression Eq. (20) and the corresponding Schrödinger equation for the solute would be nonlinear [25, 66].

B. Comparison with other treatments

We now compare our effective Hamiltonian and energy expression with previous work on similar systems. We do not attempt to review the many approaches that have been taken towards incorporating medium effects into electronic structure calculations, but rather focus on a few studies that address the problem in which we are interested: a small, highly polarisable solute dissociating inside a polarisable solvent or cluster.

One popular approach is to treat the solvent as a dielectric continuum. [23–25, 28, 66, 67]. Kim and Hynes [25] have developed a variational expression, based upon a multiconfiguration self-consistent field wavefunction, for the free energy of an interacting solute-solvent system. We consider here only the adiabatic limit (referred to by Kim and Hynes as the "Born-Oppenheimer limit") of this theory, in which the solvent electronic polarisation is regarded as fast compared with the electronic degrees of freedom of the solute. In the adiabatic limit an effective Hamiltonian for the solute may be obtained by minimising the free-energy expression with respect to the solvent electronic polarisation. This leads to an effective free energy operator for the solute, G^{BO}, which may be written in terms of our generalised solute potential $\hat{v}$ as

$$
\begin{aligned}
\hat{G}^{\mathrm{BO}} = {} & \hat{h}^C + G^{\mathrm{or}} \\
& + \left[1 + 4\pi\chi^{\mathrm{el}}\right]^{-1} \hat{\mathbf{v}} \cdot \mathsf{P}^{\mathrm{or}}(\mathsf{r}) \\
& - \frac{1}{2}\left[4\pi + \chi^{\mathrm{el}-1}\right]^{-1} \hat{\mathbf{v}} \cdot \hat{\mathbf{v}}
\end{aligned}
\tag{22}
$$

where G^{or} is the internal free energy of the solvent including the self-energy and solvent-solvent interactions, χ^{el} is the solvent electronic susceptibility, and $\mathsf{P}^{\mathrm{or}}(\mathsf{r})$ is the orientational

polarisation of the solvent. In dielectric continuum models the only solvent multipoles are dipoles, so the generalised solute potential $\hat{v}$ is proportional to the electric field arising from the solute at each point in the solvent. To aid in comparison with continuum solvent models, we rewrite our effective Hamiltonian [Eq. (15)] as

$$\hat{h}^{\text{eff}} = \hat{h}^C + E^{\text{solv}}$$
$$+ \hat{\mathbf{v}} \cdot [1 + \alpha \cdot \mathsf{T}]^{-1} \cdot \mathsf{Q}$$
$$- \frac{1}{2}\hat{\mathbf{v}} \cdot \left[\mathsf{T} + \alpha^{-1}\right]^{-1} \cdot \hat{\mathbf{v}} \tag{23}$$

where we have made use of the identity

$$\mathsf{T} \cdot [1 + \alpha \cdot \mathsf{T}]^{-1} = -\mathsf{T} \cdot \left[\mathsf{T} + \alpha^{-1}\right]^{-1} \cdot \mathsf{T} + \mathsf{T} \tag{24}$$

There is a close correspondence between the free-energy operator and the Hamiltonian, as expected. G^{or} corresponds to the internal energy of the solvent, E^{solv}, χ^{el} corresponds to the solvent polarisability $\boldsymbol{\alpha}$, and $\mathsf{P}^{\text{or}}(\mathsf{r})$ corresponds to the permanent solvent multipoles Q. The free-energy operator and the Hamiltonian exhibit the same dependence on the solvent polarisability, and both involve the *square* of the solute-potential *operator*, rather than the square of its expectation value, reflecting the importance of electronic fluctuations within the solute. It can be shown [67] that the factor 4π in $\hat{G}^{\text{BO}}$ arises from the mutual interaction between induced solvent dipoles, and plays the role of the interaction tensor T in $\hat{h}^{\text{eff}}$.

Most previous treatments of the photodissociation of solvated ions have described the solute charge distribution in terms of an empirical, localised basis. For example, the charge distribution for the basis function $|\mathrm{I}^- \ldots \mathrm{I}\rangle$ is modelled by a single point charge at the I^- nucleus, and the transition multipoles $\langle \mathrm{I}^- \ldots \mathrm{I}|\hat{q}|\mathrm{I} \ldots \mathrm{I}^- \rangle$ are set to zero. From our point of view this model amounts to a monopole approximation to the distributed multipole expansion. Studies of the energetics [13, 26] and ground-state dynamics [9, 14] of I_2^- in clusters and in solution combined this description of the charge distribution with empirical potential energy curves of the isolated solute. Localised basis functions (implied by use of a tight binding Hamiltonian) have also been used by Garcia, Bennemann and coworkers to study

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the dynamics of ionised Hg_n clusters [68,69]. However, in their approach, the solute electric field operator is replaced by its expectation value, so that their model corresponds to the "self-consistent" limit in which solute fluctuations are neglected [25, 67], rather than to the adiabatic limit used here.

The earliest dynamical studies [9,14] were restricted to the ground state potential energy surface of the solute-solvent system. Batista and Coker [32, 34] have gone beyond this restriction to simulate the adiabatic and nonadiabatic photodissociation dynamics of I_2Xe_n and $I_2^-Ar_n$ on multiple electronic surfaces, using an effective Hamiltonian based on the Diatomics-in-Ionic-Systems (DIIS) model of Last and George [35]. The DIIS model augments a semiempirical Diatomics-in-Molecules Hamiltonian with an operator that represents the strong coulombic interaction of the ionic solute with the electronic polarisability of the solvent. The resulting effective Hamiltonian operator is essentially the same as our effective Hamiltonian [Eq. (15)], although the derivation and perspective are very different. Our model differs from theirs primarily in the choice of solute basis functions. Batista and Coker expand the solute wavefunction in a basis of empirical, localised functions such as the $|I^-\ldots I\rangle$ function described above. The charge distribution corresponding to each basis function is approximated by a single point charge at the I^- nucleus, and off-diagonal matrix elements such as $\langle I^-\ldots I|\hat{v}|I\ldots I^-\rangle$ are set to zero. As a consequence of these approximations the the solute multipole and potential operators, $\hat{q}$ and $\hat{v}$, are diagonal in the localised basis.

These semiempirical, localised-basis approaches capture the dominant features of an ionic charge distribution. However, while empirical solute potential curves may be reasonably accurate, empirical charge distributions are invariably rather crude, especially at shorter bond lengths. For instance, a single point-charge may adequately describe the charge distribution of $|I^-\ldots I\rangle$ near dissociation, but it becomes an increasingly poor approximation at shorter bond lengths. The neglect of matrix elements of the multipole operators that are off-diagonal in the localised basis, which is essentially equivalent to neglect of the overlap between the basis functions, may also be expected to be inaccurate at short internuclear distances. These approximations introduce significant errors into the solvated potential surfaces in the neigh-

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bourhood of the equilibrium bond length. While it is not easy to predict their effect on the photodissociation dynamics, some of the most interesting properties of solvated ions, such as anomalous charge switching on excited states [15, 16], are sensitive to the details of the solute charge distribution at the equilibrium bond length. In contrast, ab initio wavefunctions may be used to calculate multipoles to any order, enabling one to build up an accurate representation of the potential arising from the solute charge distribution. High-level ab initio calculations may also be applied to molecules with complicated electronic structure, where a semiempirical valence-bond type wavefunction may not be adequate.

C. Validity of the adiabatic approximation

The adiabatic approximation is only valid if the solvent fluctuates at a significantly higher frequency than the solute [25]. Ideally the solute energy levels consist of a narrow spectral envelope that is quasi-degenerate with the ground state and well separated from the more highly excited states. Transitions between states within this envelope give rise to low frequency fluctuations that may be treated adiabatically.

Since it is not always immediately clear whether the adiabatic separation applies, we now consider the variation of the dispersion energy with the fluctuation frequency of the solute. For simplicity we use a perturbative approach. Although this will not give quantitative results for systems exhibiting large fluctuations, it is sufficient to determine whether the adiabatic approximation may be used.

The solvent's response to a fluctuating field is proportional to its frequency-dependent polarisability, $\alpha(\omega)$. To demonstrate this we note that the usual perturbative formula for the dispersion energy [31] between two molecules A and B may be written as

$$
\begin{aligned}
E^{\text{dispersion}} = \\
-\frac{1}{2}\sum_{i\in A}' T^{BA}\langle 0|\hat{Q}^A|i\rangle\langle i|\hat{Q}^A|0\rangle T^{AB}\alpha^{BB}\left(\Delta E_{0i}^A\right) \\
-\frac{1}{2}\sum_{j\in B}' T^{AB}\langle 0|\hat{Q}^B|j\rangle\langle j|\hat{Q}^B|0\rangle T^{BA}\alpha^{AA}\left(\Delta E_{0j}^B\right).
\end{aligned}
\tag{25}
$$

The first term of this expression contains fluctuations due to molecule A and the frequency-dependent polarisability of molecule B, while in the second term the roles of molecules A and B are reversed. The fluctuations arising from molecule A, $\langle 0|\hat{Q}^A|i\rangle\langle i|\hat{Q}^A|0\rangle$, occur at frequencies ΔE_{0i}^A corresponding to electronic transitions from the ground state to excited states $|i\rangle$. The response of molecule B is proportional to $\alpha^{BB}(\Delta E_{0i}^A)$, its polarisability at the characteristic frequency for fluctuations in the other molecule. At zero frequency $\alpha^{BB}(\omega)$ is equal to the static polarisability. As ω increases, $\alpha^{BB}(\omega)$ increases monotonically until it diverges at the first electronic transition frequency of molecule B. The formula given above is not valid at the resonant frequency, but we are chiefly concerned with the lower frequencies that characterise the solute.

At low frequencies, the frequency-dependent polarisabilities may be replaced by static polarisabilities, in which case the above expression reduces to a perturbative approximation to the adiabatic limit. (A more elaborate approach, using quasi-degenerate perturbation theory to treat the near-degenerate states of the solute, yields a similar result, as discussed in Appendix B.) More generally, the adiabatic separation may be used whenever the solvent's frequency-dependent polarisability is approximately equal to its static polarisability over the range of fluctuation frequencies exhibited by the solute.

As an example we consider the solute I_2^-, in the solvents argon, carbon-dioxide, water, ammonia and benzene. We expand the wavefunction of solvated I_2^- in a basis consisting of the six lowest states of isolated I_2^-. The solute fluctuates at frequencies corresponding to electronic excitations, and the highest electronic excitation in the six-state model [15] occurs at 3 eV. As the frequency is increased from 0 eV to 3 eV, the polarisabilities of argon [70], carbon dioxide [71], and water [72] increase by 3–4%, while ammonia [72] and benzene [73] show a 6–7% increase. The adiabatic approximation to the dispersion energy will be in error by roughly 3–7%, and this is accurate enough for most purposes.

The error introduced by the adiabatic approximation increases rapidly with the frequency of the solute fluctuations. At 5.5 eV the polarisabilities of argon, carbon dioxide and water are 13–19% greater than their static values, and the polarisabilities of ammonia and benzene

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have increased by 42–46%.

V. SUMMARY AND CONCLUSION

We have derived an effective Hamiltonian for the electronic structure of a solute interacting with an assembly of polarisable solvent molecules. The potential surfaces for an envelope of solute electronic states are determined by diagonalising the effective Hamiltonian matrix in a basis of low-lying electronic states of the isolated solute. Coulombic interactions between the solute and the solvent are assumed to dominate the potential surfaces, which is appropriate for both ionic systems and highly polar systems. Distributed multipoles are used to describe the solute charge density operator and the solvent's permanent charge distribution, while distributed polarisabilities describe the electronic polarisation of the solvent. Short range interactions arising from overlap of molecular charge distributions are treated empirically.

The effective Hamiltonian consists of the five terms given in Equation 16: E^{intra} describes the solvent internal degrees of freedom, and is taken to be zero for the case of rigid molecules; $\hat{h}^{C}$, the Hamiltonian of the isolated solute, is a diagonal matrix containing the potential surfaces of the isolated solute basis states; $\hat{h}^{\mathrm{sr}}$ incorporates the short-range forces arising from overlapping molecular charge densities and is fitted to reproduce the known features of the experimental potentials; $\frac{1}{2}(\mathsf{Q} + \hat{\mathsf{q}}) \cdot (\mathsf{V} + \hat{\mathsf{v}})$ contains the interactions of the solute and solvent charge densities with the potential created by the permanent multipole moments of the solvent; and $-\frac{1}{2}(\mathsf{V} + \hat{\mathsf{v}}) \cdot \boldsymbol{\chi} \cdot (\mathsf{V} + \hat{\mathsf{v}})$ represents interactions of the solute and solvent charge densities with the electronic polarisation of the solvent, which is assumed to respond instantaneously to fluctuations of the valence solute electrons.

The form of the effective Hamiltonian allows a detailed potential model of the solute-solvent system to be constructed from high-level ab initio calculations of the ground and excited state wavefunctions of the isolated solute. It is not necessary to assume a particular form (e.g. valence bond) for the solute wavefunction. Preliminary applications to photodis-

sociation of I_2^- in clusters of argon and carbon dioxide have shown good agreement with experiment and have deepened our understanding of the underlying dynamics [15, 16, 40]. A major finding of these studies has been that the dynamics on the excited states depends strongly on the direction of charge localisation, which undergoes a fundamental shift as the molecule dissociates because of the strong state mixing induced by spin-orbit coupling. These results indicate that a high-level description of the solute wavefunction is required for an accurate description of the solute-solvent interactions and the resulting dynamics. Further applications to these and other systems are underway and should help to increase our understanding of simple chemical reactions in clusters and condensed phases.

ACKNOWLEDGMENTS

APPENDIX A: SELF-CONSISTENT FIELD TREATMENT OF SOLVENT POLARIZATION

As remarked in section II B, the expression for the induction energy of the solvent is based upon a Hartree approximation for the solvent electronic wavefunction. In this appendix we explore this point of view in more detail, by showing how Eq.'s (14) and (15) follow when the Hartree equations are linearised. This provides an alternative derivation of the effective Hamiltonian that is more explicitly "molecular" in character than the derivation in the main text, which was patterned after theories that describe the solvent as a dielectric continuum.

We begin by considering the solvent on its own. In the Hartree approximation the solvent wavefunction takes the form

$$|\Psi^{\text{scf}}\rangle = \prod_A |\overline{\psi}^A\rangle. \tag{A1}$$

The energy is then given as the expectation value of the solvent Hamiltonian

$$\langle \Psi^{\mathrm{scf}}|\hat{H}|\Psi^{\mathrm{scf}}\rangle = \sum_A \langle \overline{\psi}^A|\hat{H}^A|\overline{\psi}^A\rangle + \frac{1}{2}\sum_{AB}\overline{Q}^A T^{AB}\overline{Q}^B \tag{A2}$$

where the average moments $\overline{Q}^A$ are expectation values of the multipole operators in the single-molecule scf states $|\overline{\psi}^A\rangle$. Minimizing the energy with the constraint that the scf states remain normalised yields the Hartree equations

$$\left[\hat{h}^A + \sum_{B\neq A}\overline{Q}^B T^{BA}\hat{Q}^A\right]|\overline{\psi}^A\rangle = \overline{\epsilon}_A|\overline{\psi}^A\rangle. \tag{A3}$$

In an scf treatment the total energy is not simply the sum of the single-molecule scf energies, since one must correct for double-counting of the interaction term

$$\overline{E} = \sum_A \overline{\epsilon}_A - \frac{1}{2}\sum_{AB}\overline{Q}^A T^{AB}\overline{Q}^B. \tag{A4}$$

Since the induced moments are determined by the difference between scf wavefunctions and the wavefunctions of the isolated molecules, the Hartree equation is an implicit self-consistency condition relating the permanent and induced moments. In general this relation will be nonlinear. The linear approximation may be derived by applying perturbation theory to the Hartree equations (Note that this approach is not equivalent to applying perturbation theory directly to the Hamiltonian, which neglects the mutual interaction between induced multipoles,resulting in the susceptibility χ being replaced by the molecular polarizability α. However, the self-consistent result can be recovered by summing a subset of terms in the perturbation series to infinite order [44].) From the first-order perturbed wavefunction

$$|\overline{\psi}_0^A\rangle \approx |\psi_0^A\rangle - \sum_{m\neq 0}|m\rangle \frac{1}{\epsilon_m^A - \epsilon_0^A}\sum_B \overline{Q}^B T^{BA}\langle m|\hat{Q}^A|0\rangle, \tag{A5}$$

we find that the average moments are given, to first order, by

$$\overline{Q}^A = Q^A - 2\sum_B \left(\sum_{m\neq 0}\frac{\langle 0|\hat{Q}^A|m\rangle\langle m|\hat{Q}^A|0\rangle}{\epsilon_m^A - \epsilon_0^A}\right)\overline{Q}^B T^{BA}$$

$$= Q^A - \sum_B \alpha^{AA}T^{AB}\overline{Q}^B. \tag{A6}$$

where we have recognised the sum-over-states formula for a molecular polarizability α. This is equivalent to the linear response equation, Eq. (9).

To complete the calculation of the scf energy we need the expectation values of the isolated molecule Hamiltonians in the scf states, which are

$$\langle \overline{\psi}_n^A | \hat{H}^A | \overline{\psi}_n^A \rangle = \epsilon_n + \frac{1}{2} \sum_{BD} \overline{Q}^B T^{BA} \alpha^{AA} T^{AD} \overline{Q}^D. \tag{A7}$$

(Since this term is second order in $\delta|\psi\rangle$, it is necessary to correct the normalization of the first-order wavefunctions when deriving it.) Combining these expressions, one arrives at an expression for the total energy in the linearised Hartree approximation that is equivalent to Eq. (11). Thus, the classical expression for the induction energy, correct to all orders in the polarization provided that the linear response approximation is valid, can be derived by making a Hartree ansatz for the quantum-mechanical wavefunction and then linearizing the resulting Hartree equations.

To extend this procedure to the solute-solvent system in the limit where the electronic polarization fluctuations are "fast" compared with the time scale for charge flow within the solute, we simply restore the remaining terms in Eq. (2) and average the Hamiltonian over an scf wavefunction for the solvent, leaving the solute variables as operators:

$$\hat{H}^C \equiv \hat{h}^c + \sum_A \langle \overline{\psi}_n^A | \hat{H}^A | \overline{\psi}_n^A \rangle + \frac{1}{2} \overline{Q} \cdot T \cdot \overline{Q} + \hat{q} \cdot T \cdot \overline{Q}. \tag{A8}$$

This, of course, is just the Born-Oppenheimer approximation, applied to two sets of *electronic* degrees of freedom rather than to electronic and nuclear degrees of freedom [23–25]. The full Hamiltonian is averaged over the fast solvent polarization fluctuations, yielding an effective Hamiltonian for the solute electrons. The linear response equation for the solvent multipoles acquires an additional source term representing the electric field generated by the solute

$$\overline{Q}^A = Q^A - \sum_B \alpha^{AA} T^{AB} \overline{Q}^B - \alpha^{AA} T^{AC} \hat{q}^C, \tag{A9}$$

which may be formally inverted to give

$$\overline{Q} + \hat{q} = [1 + \alpha \cdot T]^{-1} \cdot (Q + \hat{q}). \tag{A10}$$

The self-energy of solvent molecule A is given by a similar extension of Eq. (A7)

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$$\langle \overline{\psi}_n^A | \hat{H}^A | \overline{\psi}_n^A \rangle = \epsilon_A + \frac{1}{2} \sum_{BD} \overline{Q}^B T^{BA} \alpha^{AA} T^{AD} \overline{Q}^D$$
$$+ \sum_B \overline{Q}^B T^{BA} \alpha^{AA} T^{AC} \hat{q}^C$$
$$+ \frac{1}{2} \hat{q}^C T^{CA} \alpha^{AA} T^{AC} \hat{q}^C. \tag{A11}$$

Inserting this self-energy expression into the averaged hamiltonian, Eq. (A8), and eliminating the average moments $\overline{Q}$ using the linear response relation Eq. (A10), we arrive at an expression for the effective solute hamiltonian:

$$\hat{h}^{\mathrm{eff}} = \hat{h}^C + \sum_A \epsilon_A$$
$$+ \frac{1}{2} (\mathsf{Q} + \hat{\mathsf{q}}) \cdot \mathsf{T} \cdot [1 + \alpha \cdot \mathsf{T}]^{-1} \cdot (\mathsf{Q} + \hat{\mathsf{q}}), \tag{A12}$$

which can be rearranged to give Eq. (15). (Note that $\hat{\mathsf{q}} \cdot \mathsf{T} \cdot \hat{\mathsf{q}}$ vanishes since all components of T^{CC} are zero.)

APPENDIX B: PERTURBATIVE DERIVATION OF THE EFFECTIVE HAMILTONIAN

In this section we examine more closely the adiabatic separation of solute and solvent electronic degrees of freedom by constructing an effective Hamiltonian in which the respective time scales appear explicitly. Our approach is a direct generalization of the traditional theory of long-range intermolecular forces [45], which is based upon nondegenerate perturbation theory, to systems in which one molecule has several low-lying electronic states which may be strongly mixed by even a weak interaction with the solvent. The natural tool for dealing with such problems is quasidegenerate perturbation theory [74]. This approach is more cumbersome and less powerful than the variational argument used in Section II, but in some respects it is more straightforward and it provides a different perspective, in that the adiabatic approximation is made after the effective Hamiltonian has been derived rather than assumed at the outset.

Since quasidegenerate perturbation theory is discussed in standard textbooks on quantum theory [75] as well as in review articles [74], we omit the details of its application to our system and simply summarise the procedure here. We use the transformation approach pioneered by Van Vleck [75]. The ground and first few excited states of our solute molecule are coupled together through their interaction with the solvent. Electronic polarization of the solvent comes in through the involvement of excited electronic states of the solvent in this interaction. We wish to construct a canonical transformation that eliminates the direct coupling between solute and excited solvent states, replacing it with an effective potential that couples together the electronic states of the solute. Van Vleck perturbation theory provides a series expansion for the generating function of this transformation. Applied to the full solvent-solute Hamiltonian, eq. 2, and carried to second order, the transformation gives:

$$\hat{H}^{vv} = \hat{h}^c + E^{\text{intra}} + \frac{1}{2}\mathsf{Q} \cdot \mathsf{T} \cdot \mathsf{Q} + \hat{\mathsf{q}} \cdot \mathsf{T} \cdot \mathsf{Q} + \hat{\mathsf{V}}^{(2)} \tag{B1}$$

where the second-order effective potential $\hat{V}^{(2)}$ has the following matrix elements in the eigenstates $|n\rangle$ of the isolated solute:

$$\langle\, n\, |V^{(2)}|n'\rangle = \sum_{AB}\langle n|\hat{q}^C|n'\rangle T^{CA}X^A_{n',n,n,n}T^{AC}T^{AB}Q^B$$

$$-\frac{1}{2}\sum_A\sum_{n''}\langle n|\hat{q}^C|n''\rangle T^{CA}X^A_{n'',n,n'',n'}T^{AC}\langle n''|\hat{q}^C|n'\rangle. \tag{B2}$$

Here

$$X^A_{n'',n,n'',n'} \equiv \mathcal{A}^{AA}(\epsilon^C_{n''} - \epsilon^C_n) + \mathcal{A}^{AA}(\epsilon^C_{n''} - \epsilon^C_{n'}) \tag{B3}$$

and the response functions $\mathcal{A}(E)$ are defined in terms of sums over the excited electronic states $|m\rangle$ of the solvent molecules:

$$\mathcal{A}^{A_k A_l}_{uu'}(E) \equiv \sum_{m\neq 0}\frac{\langle 0|\hat{Q}^{A_k}_u|m\rangle\langle m|\hat{Q}^{A_l}_{u'}|0\rangle}{E + \epsilon^A_m - \epsilon^A_0}. \tag{B4}$$

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The $\mathcal{A}$ functions are related to the frequency-dependent electronic polarizabilities of the solvent molecules:

$$\alpha(\omega) = \mathcal{A}(\omega) + \mathcal{A}(-\omega). \tag{B5}$$

We now pass to the adiabatic limit, in which solute energy level spacings are assumed to be small in comparison to energy level spacings in the solvent. In this limit the frequency-dependent response functions are replaced by static polarizabilities, $\mathcal{A}(\omega) \rightarrow \frac{1}{2}\alpha$, and Eq. (B1) reduces to:

$$\begin{aligned}
\hat{h}^{\text{eff}} = {} & E^{\text{intra}} + \hat{h}^C + \hat{h}^{\text{sr}} \\
& + \frac{1}{2}\mathsf{Q} \cdot \mathsf{T} \cdot \mathsf{Q} + \hat{\mathsf{q}} \cdot \mathsf{T} \cdot \mathsf{Q} \\
& - \frac{1}{2}\left(\mathsf{Q} + \hat{\mathsf{q}}\right) \cdot \mathsf{T} \cdot \boldsymbol{\alpha} \cdot \mathsf{T} \cdot \left(\mathsf{Q} + \hat{\mathsf{q}}\right).
\end{aligned} \tag{B6}$$

This differs from the adiabatic effective Hamiltonian derived in section 2 in that the polarizability $\boldsymbol{\alpha}$ appears instead of the susceptibility $\boldsymbol{\chi} = \boldsymbol{\alpha} \cdot [1 + \mathsf{T} \cdot \boldsymbol{\alpha}]^{-1}$. The perturbative treatment considers only the direct interaction between the solute and the polarizable solvent, whereas the variational treatment accounts for the modification of this interaction by the mutual interaction of the induced solvent multipoles. Presumably such many-body corrections could also be incorporated into the frequency-dependent effective potential, Eq. (B2), but we have not pursued this in depth. In general, we expect that as long as the solvent polarizability at frequencies corresponding to the gaps between the low-lying electronic states of the solute differs little from its static limit, the adiabatic effective Hamiltonian will be valid.

REFERENCES

[1] PAPANIKOLAS, J., GORD, J., LEVINGER, N., RAY, D., VORSA, V., and LINEBERGER, W., 1991, *J. Phys. Chem.*, **95**, 8028.

[2] PAPANIKOLAS, J., VORSA, V., NADAL, M., CAMPAGNOLA, P., BUCHENAU, H., and LINEBERGER, W., 1993, *J. Chem. Phys.*, **99**, 8733.

[3] VORSA, V., CAMPAGNOLA, P. J., NANDI, S., LARSSON, M., and LINEBERGER, W. C., 1996, *J. Chem. Phys.*, **105**, 2298.

[4] VORSA, V., NANDI, S., CAMPAGNOLA, P. J., LARSSON, M., and LINEBERGER, W. C., 1997, *J. Chem. Phys.*, **106**, 1402.

[5] GREENBLATT, B. J., ZANNI, M. T., and NEUMARK, D. M., 1997, *Science*, **276**, 1675.

[6] KLINER, D. A. V., ALFANO, J. C., and BARBARA, P. F., 1993, *J. Chem. Phys.*, **98**, 5375.

[7] ALFANO, J., KIMURA, Y., WALHOUT, P., and BARBARA, P., 1993, *Chem. Phys.*, **175**, 147.

[8] WALHOUT, P. K., ALFANO, J. C., THAKUR, K. A. M., and BARBARA, P. F., 1995, *J. Phys. Chem.*, **99**, 7568.

[9] BENJAMIN, I., BARBARA, P. F., GERTNER, B. J., and HYNES, J. T., 1995, *J. Phys. Chem.*, **99**, 7557.

[10] BANIN, U., WALDMAN, A., and RUHMAN, S., 1992, *J. Chem. Phys.*, **96**, 2416.

[11] BANIN, U. and RUHMAN, S., 1993, *J. Chem. Phys.*, **98**, 4391.

[12] BANIN, U., KOSLOFF, R., and RUHMAN, S., 1994, *Chem. Phys.*, **183**, 289.

[13] MASLEN, P. E., PAPANIKOLAS, J. M., FAEDER, J., PARSON, R., and ONEIL, S. V.,

1994, *J. Chem. Phys.*, **101**, 5731.

[14] PAPANIKOLAS, J. M., MASLEN, P. E., and PARSON, R., 1995, *J. Chem. Phys.*, **102**, 2452.

[15] FAEDER, J., DELANEY, N., MASLEN, P., and PARSON, R., 1997, *Chem. Phys. Lett.*, **270**, 196.

[16] DELANEY, N., FAEDER, J., MASLEN, P. E., and PARSON, R., 1997, *J. Phys. Chem. A*, **101**, 8147.

[17] PERERA, L. and AMAR, F. G., 1989, *J. Chem. Phys.*, **90**, 7354.

[18] AMAR, F. G. and PERERA, L., 1991, *Z. Phys. D*, **20**, 173.

[19] BENJAMIN, I., BANIN, U., and RUHMAN, S., 1993, *J. Chem. Phys.*, **98**, 8337.

[20] BENJAMIN, I. and WHITNELL, R. M., 1993, *Chem. Phys. Lett.*, **204**, 45.

[21] CHEN, E. C. M. and WENTWORTH, W. E., 1985, *J. Phys. Chem.*, **89**, 4099.

[22] BUCKINGHAM, A. D., FOWLER, P. W., and STONE, A. J., 1986, *Internat. Rev. Phys. Chem.*, **5**, 107.

[23] GEHLEN, J. N., CHANDLER, D., KIM, H. J., and HYNES, J. T., 1992, *J. Phys. Chem.*, **96**, 1748.

[24] MARCUS, R. A., 1992, *J. Phys. Chem.*, **96**, 1753.

[25] KIM, H. J. and HYNES, J. T., 1992, *J. Chem. Phys.*, **96**, 5088.

[26] GERTNER, B. J., ANDO, K., BIANCO, R., and HYNES, J. T., 1994, *Chem. Phys.*, **183**, 309.

[27] BIANCO, R., TIMONEDA, J. J. I., and HYNES, J. T., 1994, *J. Phys. Chem.*, **98**, 12103.

[28] BIANCO, R. and HYNES, J. T., 1995, *J. Chem. Phys.*, **102**, 7864.

[29] BIANCO, R. and HYNES, J. T., 1995, *J. Chem. Phys.*, **102**, 7885.

[30] ATKINS, P. W., 1983, *Molecular Quantum Mechanics* (Oxford).

[31] MAITLAND, G. C., RIGBY, M., SMITH, E. B., and WAKEHAM, W. A., 1981, *Inter-molecular Forces, Their Origin and Determination* (Clarendon).

[32] BATISTA, V. S. and COKER, D. F., 1997, *J. Chem. Phys.*, **106**, 7102.

[33] BATISTA, V. S. and COKER, D. F., 1996, *J. Chem. Phys.*, **105**, 4033.

[34] BATISTA, V. S. and COKER, D. F., 1997, *J. Chem. Phys.*, **106**, 6923.

[35] LAST, I. and GEORGE, T. F., 1987, *J. Chem. Phys.*, **86**, 3787.

[36] TULLY, J. C., 1990, *J. Chem. Phys.*, **93**, 1061.

[37] HAMMES-SCHIFFER, S. and TULLY, J. C., 1994, *J. Chem. Phys.*, **101**, 4657.

[38] COKER, D. F. and XIAO, L., 1995, *J. Chem. Phys.*, **102**, 496.

[39] COKER, D. F., 1993, *Computer Simulation in Chemical Physics*, edited by ALLEN, M. P. and TILDESLEY, D. J., (Kluwer), pp. 315–377.

[40] FAEDER, J. and PARSON, R., *J. Chem. Phys.*, in press.

[41] FAEDER, J., MASLEN, P. E., and PARSON, R., to be submitted.

[42] STONE, A. J., 1981, *Chem. Phys. Lett.*, **83**, 233.

[43] STONE, A. J. and ALDERTON, M., 1985, *Mol. Phys.*, **56**, 1047.

[44] STONE, A. J., 1989, *Chem. Phys. Lett.*, **155**, 102.

[45] STONE, A. J., 1996, *The Theory of Intermolecular Forces* (Oxford).

[46] HUNTER, C. A., SANDERS, J. K. M., and STONE, A. J., 1989, *Chem. Phys.*, **133**,

395.

[47] PRICE, S. L., STONE, A. J., and ALDERTON, M., 1984, *Mol. Phys.*, **52**, 987.

[48] GREENGARD, L. and ROKHLIN, V., 1987, *J. Comput. Phys.*, **73**, 325.

[49] GREENGARD, L., 1988, *The Rapid Evaluation of Potential Fields in Particle Systems* (MIT Press).

[50] WHITE, C. A. and HEAD-GORDON, M., 1994, *J. Chem. Phys.*, **101**, 6593.

[51] STONE, A. J. and TOUGH, R. J. A., 1984, *Chem. Phys. Lett.*, **110**, 123.

[52] WHITE, C. A., JOHNSON, B. G., GILL, P. M. W., and HEAD-GORDON, M., 1994, *Chem. Phys. Lett.*, **230**, 8.

[53] STONE, A. J., 1985, *Mol. Phys.*, **56**, 1065.

[54] MASLEN, P. E., FAEDER, J., and PARSON, R., 1996, *Chem. Phys. Lett.*, **263**, 63.

[55] GRAY, C. G. and GUBBINS, K. E., 1984, *Theory of Molecular Fluids*, volume 1 (Clarendon).

[56] DYKSTRA, C. E., 1988, *Ab Initio calculations of the structures and properties of molecules* (Elsevier).

[57] MURTHY, C. S., O'SHEA, S. F., and MCDONALD, I. R., 1983, *Mol. Phys.*, **50**, 531.

[58] WEIDA, M. J. and NESBITT, D. J., 1996, *J. Chem. Phys.*, **105**, 10210.

[59] MOLPRO, a package of ab initio programs by H.-J. Werner and P. J. Knowles, with contributions from J. Almlöf, R. D. Amos, M. J. O. Deegan, S. T. Elbert, C. Hampel, W. Meyer, K. Peterson, R. Pitzer, A. J. Stone, and P. R. Taylor, version 94.3 (1994).

[60] THOLE, B. T., 1981, *Chem. Phys.*, **59**, 341.

[61] PRESS, W. H., TEUKOLSKY, S. A., VETTERLING, W. T., and FLANNERY, B. P.,

1992, *Numerical Recipes in C: The Art of Scientific Computing*, 2nd edition (Cambridge University Press).

[62] Zhao, Y., Arnold, C. C., and Neumark, D. M., 1993, *J. Chem. Soc. Faraday Trans.*, **89**, 1449.

[63] Zhao, Y., Yourshaw, I., Reiser, G., Arnold, C. C., and Neumark, D. M., 1994, *J. Chem. Phys.*, **101**, 6538.

[64] Truhlar, D. G., Onda, K., Eades, R. A., and Dixon, D. A., 1979, *Int. J. Quantum Chem. Symposium*, **13**, 601.

[65] Schnitker, J. and Rossky, P. J., 1987, *J. Chem. Phys.*, **86**, 3462.

[66] Thole, B. T. and van Duijnen, P. T., 1980, *Theor. Chim. Acta*, **55**, 307.

[67] Kim, H. J. and Hynes, J. T., 1990, *J. Chem. Phys.*, **93**, 5194.

[68] Garcia, M. E., Pastor, G. M., and Bennemann, K. H., 1993, *Phys. Rev. B*, **48**, 8388.

[69] Klaus, W., Garcia, M. E., and Bennemann, K. H., 1995, *Z. Phys. D*, **35**, 43.

[70] Ghosh, S. K. and Deb, B. M., 1983, *Theor. Chim. Acta*, **62**, 209.

[71] Amos, R. D., Handy, N. C., Knowles, P. J., Rice, J. E., *et al.*, 1985, *J. Phys. Chem.*, **89**, 2186.

[72] Reinsch, E.-A., 1985, *J. Chem. Phys.*, **83**, 5784.

[73] Karna, S. P., Talapatra, G. B., and Prasad, P. N., 1991, *J. Chem. Phys.*, **95**, 5873.

[74] Killingbeck, J., 1977, *Rep. Prog. Phys.*, **40**, 963.

[75] Kemble, E. C., 1958, *The fundamental principles of quantum mechanics, with elementary applications* (Dover).