Electric dipoles at ultralow temperatures

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1 General remarks

Any object with a net positive charge on one end and a net negative charge on the other end possesses an electric dipole moment. In ordinary classical electromagnetism this dipole moment is a vector quantity that can point in any direction, and is subject to electrical forces that are fairly straightforward to formulate mathematically. However, for a quantum mechanical object like an atom or molecule, the strength and orientation of the object's dipole moment can depend strongly on the object's quantum mechanical state. This is a subject that becomes relevant in low temperature molecular samples, where an ensemble of molecules can be prepared in a single internal state, as described elsewhere in this volume. In such a case, the mathematical description becomes more elaborate, and indeed the dipole-dipole interaction need not take the classical form given in textbooks. The description of this interaction is the subject of this chapter.

We approach this task in three steps: first, we introduce the *ideas* of how dipoles arise in quantum mechanical objects; second, we present a *formalism* within which to describe these dipoles; and third, we give *examples* of the formalism that illustrate some of the basic physics that emerges. The discussion will explore the possible energy states of the dipole, the field generated by the dipole, and the interaction of the dipole with another dipole. We restrict the discussion to a particular "minimal realistic model," so that the most important physics is incorporated, but the arithmetic is not overwhelming.

Although we discuss molecular dipoles in several contexts, our main focus is on polar molecules that possess a Λ doublet in their ground state. These molecules are the most likely, among diatomic molecules at least, to exhibit their dipolar character at moderate laboratory field strengths. Λ-doubled molecules have another peculiar feature, namely, their ground states possess a degeneracy even in an electric field. This means that there is more than one way for such a molecule to align with the field; the two possibilities are characterized by different angular momentum quantum numbers. This degeneracy leads to novel properties of both the orientation of a single molecule's dipole moment and the interaction between dipoles. In the examples we present, we focus on revealing these novel features.

We assume the reader has a good background in undergraduate quantum mechanics and electrostatics. In particular, the ideas of matrix mechanics, Dirac notation, and time-independent perturbation theory are used frequently. In addition, the reader should have a passing familiarity with electric dipoles and their interactions with fields and with each other. Finally, we will draw heavily on the mathematical theory of angular momentum as applied to quantum mechanics, as described in Appendix A of this volume, and in more detail in the classic treatise of Brink and Satchler [1]. When necessary, details of the structure of diatomic molecules have been drawn from Brown and Carrington's recent authoritative text [2].

2 Review of Classical Dipoles

The behavior of a polar molecule is largely determined by its response to electric fields. Classically, an electric dipole appears when a molecule has a little bit of positive charge displaced a distance from a little bit of negative charge. The dipole moment is then a vector quantity that characterizes the direction and magnitude of this displacement:

$$\vec{\mu} = \sum_{\xi} q_{\xi} \vec{r}_{\xi},$$

where the ξth charge q_{ξ} is displaced $\vec{r}_{\xi}$ from a particular origin. Because we are interested in forces exerted on molecules, we will take this origin to be the center of mass of the molecule. (Defining $\vec{\mu} = 0$ would instead identify the center of charge of the molecule – quite a different thing!) By convention, the dipole moment vector points away from the negative charges, and toward the positive charges, inside the molecule.

A molecule has many charges in it, and they are distributed in a complex way, as governed by the quantum mechanical state of the molecule. In general there is much more information about the electrostatic properties of the molecule than is contained in its dipole moment. However, at distances far from the molecule (as compared to the molecule's size), these details do not matter. The forces that one molecule exerts on another in this limit is strongly dominated by the dipole moments of the two molecules. We consider in this chapter only electrically neutral molecules, so that the Coulomb force between molecules is absent. In this limit, too, the details of the dipole moment's origin are irrelevant, and we consider the molecule to be a "point dipole," whose dipole moment is characterized by a magnitude μ and a direction $\hat{\mu}$.

If a dipole $\vec{\mu}$ is immersed in an electric field $\vec{\mathcal{E}}$, its energy depends on the relative orientation of the field and the dipole, via

$$E_{el} = -\vec{\mu} \cdot \vec{\mathcal{E}}.$$

This follows simply from the fact that the positive charges will be pulled in the direction of the field, while the negative charges are pulled the other way. Thus

a dipole pointing in the same direction as the field is lower in energy than a dipole pointing in exactly the opposite direction. In classical electrostatics, the energy can continuously vary between these two extreme limits.

As an object containing charge, a dipole generates an electric field, which is given, as usual, by the gradient of an electrostatic potential, $\vec{\mathcal{E}}_{\text{molecule}} = -\vec{\nabla}\Phi(\vec{r})$. For a point dipole the potential Φ is given by

$$\Phi(\vec{r}) = \frac{\vec{\mu} \cdot \hat{r}}{r^2}, \tag{1}$$

where $\vec{r} = r\hat{r}$ denotes the point in space, relative to the dipole, at which the field is to be evaluated [3]. The dot product in (1) gives the field Φ a strong angular dependence. For this reason, it is convenient to use spherical coordinates to describe the physics of dipoles, since they explicitly record directions. Setting $\hat{r} = (\theta, \phi)$ and $\hat{\mu} = (\alpha, \beta)$ in spherical coordinates, the dipole potential becomes

$$\Phi = \frac{\mu}{r^2} \left(\cos\alpha\cos\theta + \sin\alpha\sin\theta\cos(\beta - \phi) \right). \tag{2}$$

For the most familiar case of a dipole aligned along the positive z-axis ($\alpha = 0$), this yields the familiar result $\Phi = \mu\cos\theta/r^2$. This potential is maximal along the dipole's axis ($\theta = 0$ or π), and vanishes in the direction perpendicular to the dipole ($\theta = \pi/2$).

From the results above we can evaluate the interaction potential between two dipoles. One of the dipoles generates an electric field, which acts on the other. Taking the scalar product of one dipole moment with the gradient of the dipole potential (2) due to the other, we obtain [3]

$$V_d(\vec{R}) = \frac{\vec{\mu}_1 \cdot \vec{\mu}_2 - 3(\vec{\mu}_1 \cdot \hat{R})(\vec{\mu}_2 \cdot \hat{R})}{R^3},$$

where $\vec{R} = R\hat{R}$ is the relative coordinate of the dipoles. This result is general for any orientation of each dipole, and for any relative position of the pair of dipoles. In a special case where both dipoles ar aligned along the positive z-axis, and where the vector connecting the centers-of-mass of the two dipoles makes an angle θ with this axis, the dipole-dipole interaction takes a simpler form:

$$V_d(\vec{r}) = \mu_1\mu_2 \frac{1 - 3\cos^2\theta}{R^3}. \tag{3}$$

Note that the angle θ as used here has a different meaning from the one in Eq. (2). We will use θ is both contexts throughout this chapter, hopefully without causing undue confusion. The form (3) of the interaction is useful for illustrating the most basic fact of the dipole-dipole interaction: if the two dipoles line up in a head-to-tail orientation ($\theta = 0$ or π), then $V_d < 0$ and they attract one another; whereas if they lie side-by-side ($\theta = \pi/2$), then $V_d > 0$ and they repel one another.[1]

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[1]This expression ignores a contact potential that must be associated to a point dipole to conserve lines of electric flux [3]. However, real molecules are *not* point dipoles, and the electrostatic potential differs greatly from this dipolar form at length scales inside the molecule, scales that do not concern us here.

Our main goal in this chapter is to investigate how these classical results change when the dipoles belong to molecules that are governed by quantum mechanics. In Sec. 3 we evaluate the energy of a dipole exposed to an external field; in Sec. 4 we consider the field produced by a quantum mechanical dipole; and in Sec. 5 we address the interaction between two dipolar molecules.

3 Quantum mechanical dipoles in fields

Whereas the classical energy of a dipole in a field can take a continuum of values between its minimum and maximum, this is no longer the case for a quantum mechanical molecule. In this section we will establish the spectrum of a polar molecule in an electric field, building from a set of simple examples. To start, we will define the laboratory z-axis to coincide with the direction of an externally applied electric field, so that $\vec{\mathcal{E}} = \mathcal{E}\hat{z}$. In this case, the projection of the total angular momentum on the z-axis is a conserved quantity.

3.1 Atoms

Our main focus in this chapter will be on electrically polarizable dipolar molecules. But before discussing this in detail, we first consider the simpler case of an electrically polarizable atom, namely, hydrogen. This will introduce both the basic physics ideas, and the angular momentum techniques that we will use. In this case a negatively charged electron separated a distance r from a positively charged proton forms a dipole moment $\vec{\mu} = -e\vec{r}$.

Because dipoles require us to consider directions, it is useful to cast the unit vector $\hat{r}$ into its spherical components [1]:

$$\left(\frac{x}{r} \pm i\frac{y}{r}\right) = \mp\sqrt{2}C_{1\pm1}(\theta,\phi), \quad \frac{z}{r} = C_{10}(\theta,\phi).$$

Here the C's are reduced spherical harmonics, related to the usual spherical harmonics by [1]

$$C_{kq} = \sqrt{\frac{4\pi}{2k+1}}Y_{kq},$$

and given explicitly for $k = 1$ by (Appendix A)

$$C_{1\pm1}(\theta\phi) = \mp\frac{1}{\sqrt{2}}\sin\theta e^{\pm i\phi} \quad C_{10}(\theta\phi) = \cos\theta. \tag{4}$$

In general, it is convenient to represent interaction potentials in terms of the functions C_{kq} (since they do not carry extra factors of 4π), and to use the functions Y_{kq} as wave functions in angular degrees of freedom (since they are already properly normalized, by $\langle Y_{lm}|Y_{l'm'}\rangle = \delta_{ll'}\delta_{mm'}$). Integrals involving the reduced spherical harmonics are conveniently related to the 3-j symbols of

angular momentum theory, for example:

$$\int d(\cos\theta)d\phi C_{k_1 q_1}(\theta\phi)C_{k_2 q_2}(\theta\phi)C_{k_3 q_3}(\theta\phi)$$

$$= 4\pi \begin{pmatrix} k_1 & k_2 & k_3 \\ q_1 & q_2 & k_3 \end{pmatrix} \begin{pmatrix} k_1 & k_2 & k_3 \\ 0 & 0 & 0 \end{pmatrix}.$$

The 3-j symbols, in parentheses, are related to the Clebsch-Gordan coefficients. They are widely tabulated and easily computed for applications (Appendix A).

In terms of these functions, the Hamiltonian for the atom-field interaction is

$$H_{\mathrm{el}} = -(-e\vec{r}) \cdot \vec{\mathcal{E}} = ez\mathcal{E} = er\cos(\theta)\mathcal{E} = er\mathcal{E}C_{10}(\theta). \tag{5}$$

The possible energies for a dipole in a field are given by the eigenvalues of the Hamiltonian (5). To evaluate these energies in quantum mechanics, we identify the usual basis set of hydrogenic wave functions, $|nlm\rangle$, where we ignore spin for this simple illustration:

$$\langle r, \theta, \phi | nlm \rangle = f_{nl}(r)Y_{lm}(\theta, \phi).$$

The matrix elements between any two hydrogenic states are

$$\langle nlm| -\vec{\mu} \cdot \vec{\mathcal{E}} |n'l'm'\rangle \quad = \langle er\rangle\mathcal{E} \int d(\cos\theta)d\phi Y_{lm}^* C_{10} Y_{l'm'} \tag{6}$$

$$= \langle er\rangle\mathcal{E}\sqrt{(2l+1)(2l'+1)} \begin{pmatrix} l & 1 & l' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l & 1 & l' \\ -m & 0 & m' \end{pmatrix}$$

Here $\langle er\rangle = \int r^2 dr f_{nl}(r)r f_{n'l'}$ is an effective magnitude of the dipole moment, which can be analytically evaluated for hydrogen [4].

Some important physics is embodied in Eqn. (6). First, the electric field defines an axis of rotational symmetry (here the z axis). On general grounds, we therefore expect that the projection of the total angular momentum of the molecule onto this axis is a constant. And indeed, this is built into the 3-j symbols: since the sum of all m quantum numbers in a 3-j symbol should add to zero, Eqn. (6) asserts that $m = m'$, and the electric field cannot couple two different m's together.

A second feature embodied in (6) is the action of parity. The hydrogenic wavefunctions have a definite parity, i.e., they either change sign, or else remain invariant, upon converting from a coordinate system (x, y, z) to a coordinate system $(-x, -y, -z)$. The sign of the parity-changed wave function is given by $(-1)^l$. Thus an s-state ($l = 0$) has even parity, while a p-state ($l = 1$) has odd parity. For an electric field pointing in a particular direction, the Hamiltonian (5) itself has odd parity, and thus serves to *change* the parity of the atom. For example, it can couple the s and p states to each other, but not to themselves. This is expressed in (6) by the first 3-j symbol, whose symmetry properties require that $l + 1 + l' =$ even. This seemingly innocuous statement is the *fundamental fact* of electric dipole moments of atoms and molecules. It says

that, for example the $1s$ ground state of hydrogen, with $l = l' = 0$, does not, by itself, respond to an electric field at all. Rather, it requires an admixture of a p state to develop a dipole moment.[2]

To evaluate the influence of an electric field on hydrogen, therefore, we must consider at least the nearest state of opposite parity, which is the $2p$ state. These two states are separated in energy by an amount E_{1s2p}. Considering only these two states, and ignoring any spin structure, the atom-plus-field Hamiltonian is represented by a simple 2×2 matrix:

$$H = \begin{pmatrix} -E_{1s2p}/2 & \mu\mathcal{E} \\ \mu\mathcal{E} & E_{1s2p}/2 \end{pmatrix}. \tag{7}$$

where the dipole matrix element is given by the convenient shorthand $\mu = \langle 1s, m = 0|ez|2p, m = 0\rangle = 128\sqrt{2}ea_0/243$ [4]. Of course there are many more p states that the $1s$ state is coupled to. Plus, all states are further complicated by the spin of the electron and (in hydrogen) the nucleus. Matrix elements for all these can be constructed, and the full matrix diagonalized to approximate the energies to any desired degree of accuracy. However, we are interested here in the qualitative features of dipoles, and so limit ourselves to Eqf.(7).

The Stark energies are thus given approximately by

$$E_\pm = \pm\sqrt{(d\mathcal{E})^2 + (E_{1s2p}/2)^2}. \tag{8}$$

This expression illustrates the basic physics of the quantum mechanical dipole. First, there are necessarily two states (or more) involved. One state decreases in energy as the field is turned on, representing the "normal" case where the electron moves to negative z and the electric dipole moment aligns with the field. The other state, however, increases in energy with increasing field and represents the dipole moment anti-aligning with the field. Classically it is of course possible to align the dipole against the field in a state of unstable equilibrium. Similarly, in quantum mechanics this is a legitimate energy eigenstate, and the dipole will remain anti-aligned with the field in the absence of perturbations.

A second observation about the energies (8) is that the energy is a quadratic function of $\mathcal{E}$ at low field, and only becomes linearly proportional to $\mathcal{E}$ at higher fields. Thus the permanent dipole moment of the atom, defined by the zero-field limit

$$\mu_{\text{permanent}} \equiv \lim_{\mathcal{E}\to 0} \frac{\partial E_-}{\partial \mathcal{E}},$$

vanishes. The atom, in an energy eigenstate in zero field, has no permanent electric dipole moment. This makes sense since, in zero field, the electron's position is randomly varied about the atom, lying as much on one side of the nucleus as on the opposite side.

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[2]These remarks are not strictly true. The ground state of hydrogen already has a small admixture of odd-parity states, due to the parity-violating part of the electroweak force. This effect is far too small to concern us here, however.

The transition from quadratic to linear Stark effect is an example of a competition between two tendencies. At low field, the dominant energy scale is the energy splitting E_{1s2p} between opposite parity states. At higher field values, the interaction energy with the electric field becomes stronger, and the dipole is aligned. The value of the field where this transition occurs is found roughly by setting these energies equal to find a "critical" electric field:

$$\mathcal{E}_{\text{critical}} = E_{1s2p}/2d.$$

For atomic hydrogen, this field is on the order of 10^9 V/cm. However, at this field it is already a bad approximation to ignore that fact that there are both $2p_{1/2}$ and $2p_{3/2}$ states, as well as higher-lying p states, and further coupling between p, d, etc., states. We will not pursue this subject further here.

3.2 Rotating molecules

With these basics in mind, we can move on to molecules. We focus here on diatomic, heteronuclear molecules, although the principles are more general. We will consider only electric fields so small that the electrons cannot be polarized in the sense of the previous section; thus we consider only a single electronic state. However, the charge separation between the two atoms produces an electric dipole moment $\vec{\mu}$ in the rotating frame of the molecule. We assume that the molecule is a rigid rotor and we will not consider explicitly the vibrational motion of the molecule, focusing instead solely on the molecular rotation. (More precisely, we consider $\vec{\mu}$ to incorporate an averaging over the vibrational coordinate of the molecule, much as the electron-proton distance r was averaged over for the hydrogen atom in the previous section.)

As a mathematical preliminary, we note the following. To deal with molecules, we are required to transform freely between the laboratory reference frame and the body-fixed frame that rotates with the molecule. The rotation from the lab frame (x, y, z) to the body frame (x', y', z') is governed by a set of Euler angles (α, β, γ) (Appendix A). The first two angles $\alpha = \phi$, $\beta = \theta$ coincide with the spherical coordinates (θ, ϕ) of the body frame's z' axis. By convention, we take the positive z' direction to be parallel to the dipole moment $\vec{\mu}$. The third Euler angle γ serves to orient the x' axis in a desired orientation within the body frame; it is thus the azimuthal angle of rotation about the molecular axis.

Consider a given angular momentum state $|jm\rangle$ referred to the lab frame. This state is only a state of good m in the lab frame, in general. In the body frame, which points in some other direction, the same state will be a linear superposition of different m's, which we denote in the body frame as ω's to distinguish them. Moreover, this linear superposition will be a function of the Euler angles, with a transformation that is conventionally denoted by the letter D:

$$D(\alpha\beta\gamma)|j\omega\rangle \quad = \sum_m |jm\rangle\langle jm|D(\alpha, \beta, \gamma)|j\omega\rangle$$

$$\equiv \sum_m |jm\rangle D^j_{m\omega}(\alpha, \beta, \gamma).$$

This last line defines the Wigner rotation matrices, whose properties are widely tabulated. For each j, $D^j_{m\omega}$ is a unitary transformation matrix; note that a rotation can only change m-type quantum numbers, not the total angular momentum j. One of the more useful properties of the D matrices, for us, is

$$\int d\alpha d\cos(\beta)d\gamma \qquad D^{j_1}_{m_1\omega_1}(\alpha\beta\gamma)D^{j_2}_{m_2\omega_2}(\alpha\beta\gamma)D^{j_3}_{m_3\omega_3}(\alpha\beta\gamma) =$$

$$8\pi^2 \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \begin{pmatrix} j_1 & j_2 & j_3 \\ \omega_1 & \omega_2 & m\omega_3 \end{pmatrix} \qquad (9)$$

Because the dipole is aligned along the molecular axis, and because the molecular axis is tilted at an angle β with respect to the field, and because the field defines the z-axis, the dipole moment is defined by its magnitude μ times a unit vector with polar coordinates (β, α). The Hamiltonian for the molecule-field interaction is given by

$$H_{\text{el}} = -\vec{\mu}_{\text{el}} \cdot \vec{\mathcal{E}} = -\mu\mathcal{E}C_{10}(\beta\alpha) = -\mu\mathcal{E}D^{j*}_{q0}(\alpha\beta\gamma). \qquad (10)$$

For use below, we have taken the liberty of rewriting C_{10} as a D-function; since the second index of D is zero, this function does not actually depend on γ, so introducing this variable is not as drastic as it seems.

To evaluate energies in quantum mechanics we need to choose a basis set and take matrix elements. The Wigner rotation matrices are the quantum mechanical eigenfunctions of the rigid rotor. With normalization, these wave functions are

$$\langle\alpha\beta\gamma|nm_n\lambda_n\rangle = \sqrt{\frac{2n+1}{8\pi^2}}D^{n*}_{m_n\lambda_n}.$$

As we did for hydrogen, we here ignore spin. Thus n is the quantum number of rotation of the atoms about their center of mass, m_n is the projection of this angular momentum in the lab frame, and λ_n is its projection in the body frame. In this basis, the matrix elements of the Stark interaction are computed using (9), to yield

$$\langle nm_n\lambda_n| -\vec{\mu}_{\text{el}} \cdot \vec{\mathcal{E}}|n^{'}m^{'}_n\lambda^{'}\rangle \qquad (11)$$

$$= -\mu_{\text{el}}\mathcal{E}(-1)^{m_n-\lambda_n}\sqrt{(2n+1)(2n'+1)} \begin{pmatrix} n & 1 & n^{'} \\ -m_n & 0 & m^{'}_n \end{pmatrix} \begin{pmatrix} n & 1 & n^{'} \\ -\lambda_n & 0 & \lambda^{'}_n \end{pmatrix}.$$

In an important special case, the molecule is in a Σ state, meaning that the electronic angular momentum projection $\lambda_n = 0$. In this case, Eqn. (11) reduces to the same expression as that for hydrogen, apart from the radial integral. This is as it should be: in both objects, there is simply a positive charge at one end and a negative charge at the other. It does not matter if one of these is an electron, rather than an atom. More generally, however, when $\lambda_n \neq 0$ there will be a complicating effect of lambda-doubling, which we will discuss in the next section.

Thus the physics of the rotating dipole is much the same as that of the hydrogen atom. Eqn. (11) also asserts that, for a Σ state with $\lambda_n = 0$, the electric field interaction vanishes unless n and n' have opposite parity. For such a state, the parity is related to the parity of n itself. Thus, for the ground state of a $^1\Sigma$ molecule with $n = 0$, the electric field only has an effect by mixing this state with the next rotational state with $n' = 1$. These states are split by an energy $E_{\rm rot} = 2B_e$, where B_e is the rotational constant of the molecule.[3]

We can formulate a simple 2×2 matrix describing this situation, as we did for hydrogen:

$$H = \begin{pmatrix} -E_{\rm rot}/2 & -\mu\mathcal{E} \\ -\mu\mathcal{E} & +E_{\rm rot}/2 \end{pmatrix}, \tag{12}$$

where the dipole matrix element is given by the convenient shorthand notation $\mu = \langle nm_n 0|\mu_{q=0}|n'm_n 0\rangle$. There is one such matrix for each value of m_n. Of course there are many more rotational states that these states are coupled to. Plus, all states would further be complicated by the spins (if any) of the electrons and nuclei.

The matrix (12) can be diagonalized just as (7) was above, and the same physical conclusions apply. Namely, the molecule in a given rotational state has *no permanent electric dipole moment*, even though there is a separation of charges in the body frame of the molecule. Second, the Stark effect is quadratic for low fields, and linear only at higher fields, with the transition occurring at a "critical field"

$$E_{\rm crit} = E_{\rm rot}/2\mu. \tag{13}$$

To take an example, the NH molecule posesses a $^3\Sigma$ ground state. For this state, ignoring spin, the critical field is of the order 7×10^6 V/cm. This is far smaller than the field required to polarize electrons in an atom or molecule, but still large for laboratory-strength electric fields. Diatomic molecules with smaller rotational constants, such as LiF, would have correspondingly smaller critical fields. In any event, by the time the critical field is applied, it is already a bad approximation to ignore coupling to the other rotational states of the molecule, which must be included for an accurate treatment. We do not consider this topic further here.

3.3   Molecules with lambda-doubling

As we have made clear in the previous two sections, the effect of an electric field on a quantum mechanical object is to couple states of opposite parity. For a molecule in a Π or Δ state, there are often two such parity states that are much closer together in energy than the rotational spacing. The two states are said to be the components of a "Λ-doublet." Because they are close together in energy, these two states can then be mixed at much smaller fields than are required to mix rotational levels. The physics underlying the lambda doublet is rather complex, and we refer the reader to the literature for details [2, 5].

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[3]In zero field, the state with rotational quantum number n has energy $B_e n(n + 1)$.

However, in broad terms, the argument is something like this: a Π state has an electronic angular momentum projection of magnitude 1 about the molecular axis. This angular momentum comes in two projections, for the two sense of rotation about the axis, and these projections are nominally degenerate in energy. The rotation of the molecule, however, can break the degeneracy between these levels, and (it so happens) the resulting nondegenerate eigenfunctions are also eigenfunctions of parity. The main point is that the resulting energy splitting is usually quite small, and these parity states can be mixed in fields much smaller than those required to mix rotational states.

To this end, we modify the rigid-rotor wave function of the molecule to incorporate the electronic angular momentum:

$$\langle \alpha\beta\gamma | jm\omega \rangle = \sqrt{\frac{2j+1}{8\pi^2}} D^{j*}_{m\omega}(\alpha\beta\gamma). \tag{14}$$

Here j is the *total* (rotation-plus-electronic) angular momentum of the molecule, and m and ω are the projections of j on the laboratory and body-fixed axes, respectively. Using the total j angular momentum, rather than just the molecular rotation n, marks the use of a "Hund's case a" representation, rather than the Hund's case b that was implicit in the previous section (Ref. [2]; see also Appendix B of this volume).

In this basis the matrix element of the electric field Hamiltonian (10) becomes

$$\langle jm\omega | -\vec{\mu}_{\text{el}} \cdot \vec{\mathcal{E}} | j'm'\omega' \rangle \tag{15}$$
$$= -\mu_{\text{el}}\mathcal{E}(-1)^{m-\omega}(2j+1) \begin{pmatrix} j & 1 & j' \\ -m & 0 & m' \end{pmatrix} \begin{pmatrix} j & 1 & j' \\ -\omega & 0 & \omega' \end{pmatrix}.$$

In (15), the 3-j symbols denote conservation laws. The first asserts that $m = m'$ is conserved, as we already knew. The second 3-j symbol adds to this the fact that $\omega = \omega'$. This is the statement that the electric field cannot exert a torque around the axis of the dipole moment itself. Moreover, in the present model we assert that $j = j'$, since the next higher-lying j level is far away in energy, and only weakly mixes with the ground state j. With these approximations, the 3-j symbols have simple algebraic expressions, and we can simplify the matrix element:

$$\langle jm\omega | -\vec{\mu}_{\text{el}} \cdot \vec{\mathcal{E}} | jm\omega \rangle = -\mu\mathcal{E}\frac{m\omega}{j(j+1)}.$$

The physical content of this expression is illustrated in Fig. 1. Notice that both m and ω can have a sign, and that whether the energy is positive or negative depends on both signs.

An essential point is that there is not a unique state representing the dipole aligned with the field. Rather, there are two such states, distinguished by different angular momentum quantum numbers but possessing the same energy. To distinguish these in the following we will refer to the two states in figures 1(a) and 1(b) as molecules of type $|a\rangle$ and type $|b\rangle$, respectively. Likewise, for

molecules nominally anti-aligned with the field, we will refer to types $|c\rangle$ and $|d\rangle$, corresponding to the two states in figures 1(c) and 1(d). The existence of these degeneracies will lead to novel phenomena in these kinds of molecules, as we discuss below.

As to the lambda doubling, it is, as we have asserted, diagonal in a basis where parity is a good quantum number. In terms of the basis (14), wave functions of well-defined parity are given by the linear combinations

$$|jm\bar{\omega}\epsilon\rangle = \frac{1}{\sqrt{2}}\left[|jm\bar{\omega}\rangle + \epsilon|jm\bar{\omega}\rangle\right].\qquad(16)$$

Here we define $\bar{\omega} = |\omega|$, the absolute value of ω. For a given value of m, the linear combinations of $\pm\bar{\omega}$ in (16) are distinguished by the parity quantum number $\epsilon = \pm 1$. It is straightforward to show that in the parity basis (16) the Λ-doubling is off-diagonal.

The net result is that for each value of m, the Hamiltonian for our lambda-doubled molecule can be represented as a two-by-two matrix, similar to the ones above:

$$H = \left(\begin{array}{cc} -Q & \Delta/2 \\ \Delta/2 & Q \end{array}\right),$$

where Δ is the lambda doubling energy, i.e., the energy difference between the two parity states, and

$$Q \equiv \mu\mathcal{E}\frac{|m|\bar{\omega}}{j(j+1)}$$

is a manifestly positive quantity. This is the Hamiltonian we will treat in the remainder of this chapter. The difference here from the previous subsections is that the basis is now (14), which diagonalizes the electric field interaction rather than the zero-field Hamiltonian. This change reflects our emphasis on molecules in strong fields where their dipole moments are made manifest. The zero-field Λ-doubling Hamiltonian is considered, for the most part, to be a perturbation.

The mixing of the strong field states due to the Λ-doubling interaction is conveniently given by a mixing angle δ_m, which we define as follows:

$$\begin{aligned}|m\bar{\omega}\epsilon = +\rangle &= \cos\delta_m|m\bar{\omega}\rangle + \sin\delta_m|m-\bar{\omega}\rangle \\ |m\bar{\omega}\epsilon = -\rangle &= -\sin\delta_m|m\bar{\omega}\rangle + \cos\delta_m|m-\bar{\omega}\rangle\end{aligned}\qquad(17)$$

Explicitly, the mixing angle as a function of field is given by

$$\tan\delta_{|m|} = \frac{\Delta/2}{Q + Q\sqrt{1+\eta^2}} = -\tan\delta_{-|m|},$$

in terms of the energy Q and the dimensionless parameter

$$\eta_m = \frac{\Delta}{2Q}.$$

Figure 1: Energetics of a polar molecule in an electric field. The molecule's dipole moment points from the negatively charged atom (large circle) to the positively charged atom (small circle) as indicated by the thick arrow. The dashed line indicates the positive direction of the molecules body axis, while the vertical arrow represents the direction of the applied electric field. The dipole aligns with the field, on average, if *either* i) the angular momentum $\vec{j}$ aligns with the field and $m > 0$, $\omega > 0$ (a); or ii) $\vec{j}$ aligns against the field and $m < 0$, $\omega < 0$ (b). Similar remarks apply to dipoles that anti-align with the field (c,d).
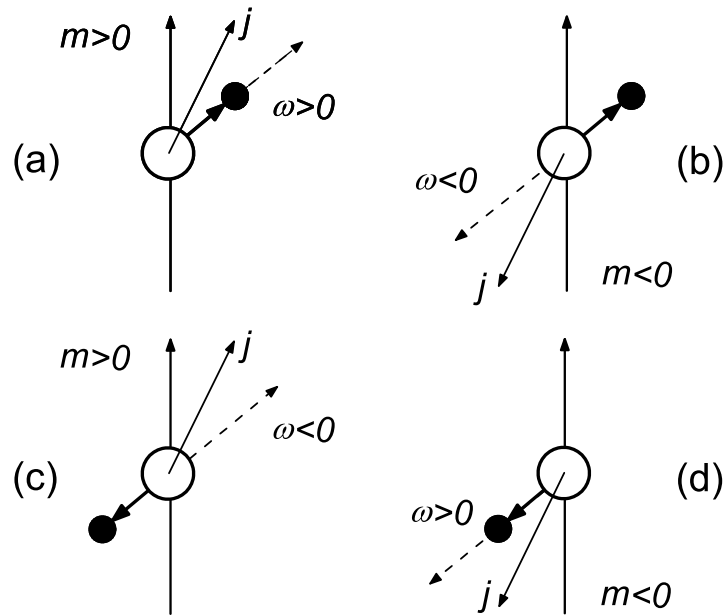
Notice that with this definition, δ_m is positive when m is positive, and $\delta_{-m} = -\delta_m$. The energies of these states are conveniently summarized by the expression

$$E_{m\bar{\omega}\epsilon} = -\mu\mathcal{E}\frac{m\epsilon\bar{\omega}}{j(j+1)}\sqrt{1+\eta^2}, \quad m \neq 0.$$

This is a very compact way of writing the results that will facilitate writing the expressions below. Notice that the intuition afforded by Figure 1 is still intact in these energies, but by replacing the sign of ϵ for the sign of ω. Thus states with $m\epsilon > 0$ have negative energy, while states with $m\epsilon < 0$ have positive energy.

The case where $m = 0$ must be handled slightly differently, since in this case the electric field energies $Q = 0$. We can still write the eigenstates in the form (17), provided that we set

$$\delta_0 = \frac{\pi}{4},$$

and understand that the corresponding energies, independent of field, are simply

$$E_{0\bar{\omega}\epsilon} = -\epsilon\Delta/2.$$

Like the dipoles considered above, this model has a quadratic Stark effect at low energies, rolling over to linear at electric fields exceeding the critical field given by setting $Q = \Delta/2$. This criterion gives a critical field of

$$E_{\mathrm{crit}} = \frac{\Delta j(j+1)}{2\mu|m|\bar{\omega}}. \tag{18}$$

To take an example, consider the ground state of OH, which has $j = \bar{\omega} = 3/2$, $\mu = 1.7$ Db, and a Λ-doublet splitting of 0.06 cm^{-1}. In its $m = 3/2$ ground state, its critical field is ~ 1600 V/cm. Again, we have explicitly ignored the spin of the electron. The parity states are therefore easily mixed in fields that are both small enough to easily obtain in the laboratory, and small enough that no second-order coupling to rotational or electronic states needs to be considered. Keeping the relatively small number of molecular states is therefore a reasonable approximation, and highly desirable as it simplifies our discussion.[4]

4   The field due to a dipole

Once polarized, each of the Λ-doubled molecules discussed above is itself the source of an electric field. The field due to a molecule is given above by Eqn. (1). In what follows, it is convenient to cast this potential in terms of the spherical tensors defined above and in Appendix A:

$$\Phi(\vec{r}) = \frac{\vec{\mu}\cdot\hat{r}}{r^2} = \frac{\mu}{r^2}\sum_q(-1)^q C_{1q}(\alpha\beta)C_{1-q}(\theta\phi), \tag{19}$$

---

[4]In OH there is also the $\bar{\omega} = 1/2$ state to consider, but it is also far away in energy as compared to the Λ-doublet, and we ignore it. It does play a role in the fine structure of OH, however, and this should be included in a quantitative model of OH.

That this form is correct can be verified by simple substitution, using the definitions (4). It seems at first unnecessarily complicated to write (19) in this way. However, the effort required to do so will be rewarded when we need to evaluate the potential for quantum mechanical dipoles below.

For a classical dipole, defining the direction $(\alpha\beta)$ of its dipole moment would immediately specify the electrostatic potential it generates according to Eq. (19). However, in quantum mechanics the potnetial will result from suitably averaging the orientation of μ over the distribution of $(\alpha\beta)$ dictated by the molecule's wave function. To evaluate this, we need to evaluate matrix elements of (19) in the basis of energy eigenstates (17). This is easily done using Eq.(9), along with formulas that simplify the 3-j symbols. The result is

$$\langle jm\omega|C_{1q}|jm'\omega'\rangle = \delta_{\omega\omega'}\frac{\omega}{j(j+1)} \left\{ \begin{array}{ll} -\sqrt{\frac{(j+m)(j-m')}{2}}, & q=+1 \\ m, & q=0 \\ +\sqrt{\frac{(j-m)(j+m')}{2}}, & q=-1 \end{array} \right\}, \qquad (20)$$

where the quantum numbers m and ω are signed quantities. Also note that this integration is over the molecular degrees of freedom $(\alpha\beta)$ in (19). This still leaves the angular dependence on $(\theta\phi)$, which characterizes the field in space around the dipole.

From expression (20) it is clear that this matrix element changes sign upon either i) reversing the sign of both m and m' or ii) changing the sign of ω. Moreover, $\langle jm\omega|C_{1q}|jm' - \omega\rangle = 0$, since ω is conserved by the electric field. Using these observations, we can readily compute the matrix elements of Φ in the dressed basis (16). Generally they take the form

$$\langle jm\bar{\omega}\epsilon|\Phi(\vec{r})|jm'\bar{\omega}\epsilon'\rangle = \langle jm\bar{\omega}\epsilon|C_{1q}|jm'\bar{\omega}\epsilon'\rangle(-1)^q \frac{\mu}{r^2} C_{1-q}(\theta\phi). \qquad (21)$$

The matrix elements in front of (21) represent the quantum mechanical manifestation of the dipole's orientation. These matrix elements follow from the above definition of the dressed states, (17). Explicitly,

$$\begin{array}{rcl} \langle jm\bar{\omega}, \epsilon|C_{1q}|jm'\bar{\omega}, \epsilon\rangle & = & \epsilon\cos(\delta_m + \delta_{m'})\langle jm\bar{\omega}|C_{1q}|jm'\bar{\omega}\rangle \\ \langle jm\bar{\omega}, -|C_{1q}|jm'\bar{\omega}, +\rangle & = & \langle jm\bar{\omega}, +|C_{1q}|jm'\bar{\omega}, -\rangle \\ & = & -\sin(\delta_m + \delta_{m'})\langle jm\bar{\omega}|C_{1q}|jm'\bar{\omega}\rangle. \end{array} \qquad (22)$$

In all these expressions, the value of q is set by angular momentum conservation to $q = m - m'$.

This description, while complete within our model, nevertheless remains somewhat opaque. Let us therefore specialize it to the case of a particular energy eigenstate $|jm\bar{\omega}\epsilon\rangle$. In this state, the averaged electrostatic potential of the dipole is

$$\langle\Phi(\vec{r})\rangle = \left(\mu\frac{m\epsilon\omega}{j(j+1)}\cos 2\delta_m\right)\frac{\cos\theta}{r^2}. \qquad (23)$$

Here the factor in parentheses is a quantum mechanical correction to the magnitude of the dipole moment. The factor $\cos 2\delta_m$, expresses the degree of polarization: in a strong field, $\delta_m = 0$ and the dipole is at maximum strength, whereas in zero field $\delta_m = \pi/4$ and the dipole vanishes. Notice that for a given value of m, the potential generated by the states with $\epsilon = \pm$ differ by a sign. this is appropriate, since these states correspond to dipoles pointing in opposite directions (Figure 1).

The off-diagonal matrix elements in (21) are also important, for two reasons. First, it may be desirable to create superpositions of different energy eigenstates, and computing these matrix elements requires the off-diagonal elements in (21), as we will see shortly. Second, when two dipoles interact with each other, one will experience the electric field due to the other, and this field need not lie parallel to the z-axis. Hence, the m quantum number of an individual dipole is no longer conserved, and elements of (21) with $q \neq 0$ are required.

4.1   Example: $j = 1/2$

To illustrate these abstract points, we consider here the simplest molecular state with a Λ doublet: a molecule with $j = 1/2$, which has $\bar{\omega} = 1/2$, and consists of four internal states in our model. Based on the discussion above, we tabulate the matrix elements between these states in Table I. Because we have $j = 1/2$, we suppress the index j in this section.

For concreteness, we focus on a type $|a\rangle$ molecule, as defined in Figure 1. This molecule aligns with the field and produces an electrostatic potential (23). However, if the molecule is prepared in a state that is a superposition of this state with another, a different electrostatic potential can result. We first note that combining $|a\rangle$ with $|b\rangle$ produces nothing new, since both states generate the same potential.

An alternative superposition combines states $|a\rangle$ with state $|c\rangle$. In this case the two states have the same value of m, but are nevertheless non-degenerate. We define

$$|\psi\rangle_{ac} = Ae^{i\omega_0 t}|\frac{1}{2}\bar{\omega}, +\rangle + Be^{-i\omega_0 t}|\frac{1}{2}\bar{\omega}, -\rangle,$$

for arbitrary complex numbers A and B with $|A|^2 + |B|^2 = 1$. Because the two states are non-degenerate, it is necessary to include the explicit time-dependent phase factors, where $\omega_0 = |E_{m\bar{\omega}\epsilon}|/\hbar$, and $2\hbar\omega_0$ is the energy difference between the states. As usual in quantum mechanics, these phases will beat against one another to make the observables time dependent.

Now some algebra identifies the mean value of the electrostatic potential, averaged over state $|\psi\rangle_{ac}$, as

$$_{ac}\langle\psi|\Phi(\vec{r})|\psi\rangle_{ac} \tag{24}$$
$$= \frac{\mu}{3r^2}\left[\left(|A|^2 - |B|^2\right)\cos 2\delta_{1/2} - 2|AB|\sin 2\delta_{1/2}\cos(2\omega_0 t - \delta)\right]\cos\theta.$$

This potential has the usual $\cos\theta$ angular dependence, meaning that the dipole remains aligned along the field's axis. However, the magnitude, and even the

Table 1: Matrix elements $\langle m\bar{\omega}\epsilon|C_{1q}|m'\bar{\omega}\epsilon'\rangle$ for a $j = 1/2$ molecule. To obtain matrix elements of the electrostatic potential $\Phi(\vec{r})$, these matrix elements should be multiplied by $(-1)^q C_{k-q}(\theta\phi)\mu/r^2$, where $q = m - m'$.

	$\lvert\frac{1}{2}\bar{\omega}+\rangle$	$\lvert\frac{1}{2}\bar{\omega}-\rangle$	$\lvert-\frac{1}{2}\bar{\omega}+\rangle$	$\lvert-\frac{1}{2}\bar{\omega}-\rangle$
$\langle\frac{1}{2}\bar{\omega}+\rvert$	$\frac{1}{3}\cos 2\delta_{1/2}$	$-\frac{1}{3}\sin 2\delta_{1/2}$	$-\frac{\sqrt{2}}{3}$	0
$\langle\frac{1}{2}\bar{\omega}-\rvert$	$-\frac{1}{3}\sin 2\delta_{1/2}$	$-\frac{1}{3}\cos 2\delta_{1/2}$	0	$\frac{\sqrt{2}}{3}$
$\langle-\frac{1}{2}\bar{\omega}+\rvert$	$\frac{\sqrt{2}}{3}$	0	$-\frac{1}{3}\cos 2\delta_{1/2}$	$-\frac{1}{3}\sin 2\delta_{1/2}$
$\langle-\frac{1}{2}\bar{\omega}-\rvert$	0	$-\frac{\sqrt{2}}{3}$	$-\frac{1}{3}\sin 2\delta_{1/2}$	$\frac{1}{3}\cos 2\delta_{1/2}$

sign, of the dipole change over time. The first term in square brackets in (24) gives a constant, dc component to the dipole moment, which depends on the population imbalance $|A|^2 - |B|^2$ between the two states. The second term adds to this an oscillating component with angular frequency $2\omega_0$. The leftover phase δ is an irrelevant offset, and comes from the phase of A^*B, i.e., the relative phase of the two components at time $t = 0$.

It is therefore possible to construct a superposition of states of the dipole, such that the effective dipole moment of the molecule bobs up and down in time. The amount that the dipole bobs, relative to the constant component, can be controlled by the relative population in the two states. Moreover, the degree of polarization of the molecule plays a significant role. For a fully polarized molecule, when $\delta_{1/2} = 0$, only the dc portion of the dipole persists, although even it can vanish if there is equal population in the two states, "dipole up" and "dipole down."

As another example, we consider the superposition of $|a\rangle$ with $|d\rangle$. Now the two states have different values of m as well as different energies:

$$|\psi\rangle_{ad} = Ae^{i\omega_0 t}\lvert\tfrac{1}{2}\bar{\omega},+\rangle + Be^{-i\omega_0 t}\lvert-\tfrac{1}{2}\bar{\omega},+\rangle.$$

The dipole potential this superposition generates is

$$\begin{aligned}
&{}_{ad}\langle\psi|\Phi(\vec{r})|\psi\rangle_{ad} \\
&= \frac{\mu}{3r^2}\cos 2\delta_{1/2}\left(|A|^2 - |B|^2\right)\cos\theta + \frac{2\mu}{3r^2}\mathrm{Re}\left[A^*Be^{-i(\phi+2\omega_0 t)}\right]\sin\theta.
\end{aligned}$$

This expression can be put in a useful and interesting form if we parametrize the coefficients A and B as

$$A = \cos\frac{\alpha}{2}e^{-i\beta/2} \quad B = \sin\frac{\alpha}{2}e^{i\beta/2}.$$

This way of writing A and B seems arbitrary, but it is not. It is the same parametrization that is used in constructing the Bloch sphere, which is a powerful tool in the analysis of any two-level system [6].

This parametrization leads to the following expression for the potential:

$$_{ad}\langle\psi|\Phi(\vec{r})|\psi\rangle_{ad} \qquad\qquad\qquad\qquad\qquad (25)$$
$$= \frac{1}{3}\frac{\mu}{r^2}\left[\cos 2\delta_{1/2}\cos\alpha\cos\theta + \sin\alpha\sin\theta\cos((\beta - 2\omega_0 t) - \phi)\right].$$

The interpretation of this result is clear upon comparing it to the classical result (2). First consider that the molecule is perfectly polarized, so that $\cos 2\delta_{1/2} = 1$. Then (25) represents the potential due to a dipole whose polar coordinates are $(\alpha, \beta - \omega t)$. That is, this dipole makes (on average) an angle α with respect to the field, and it precesses about the field with an angular frequency $2\omega_0$. Interestingly, even in this strong field limit where the field nominally aligns the dipole along z, quantum mechanics allows the dipole to point in quite a different direction. As the field relaxes, the z-component reduces, but this dipole still has a component precessing about the field.

4.2   Example: $j = 1$

We also consider a molecule with spin $j = 1$. Here there are in principle three mixing angles, δ_1, δ_0, and δ_{-1}. However, as noted above we have $\delta_{-1} = -\delta_1$ and $\delta_0 = \pi/4$, so that the entire electric field dependence of these matrix elements is incorporated in the single parameter δ_1. In this notation, the matrix elements of the electrostatic potential for a $j = 1$ molecule are given in Table 2.

Similar remarks apply to the spin-1 case as applied to the spin-1/2 case. If the molecule is in an eigenstate, say $|+1\bar{\omega}, -\rangle$, then the expectation value of the dipole points along the field axis, and its distribution has the usual $\cos\theta$ dependence. In an eigenstate with $m = 0$, however, the expectation value of the dipole vanishes altogether.

As before, the molecule can also be in a superposition state. No matter how complicated this superposition is, the expectation value of the dipole must instantaneously point in some direction, since the only available angular dependence resides in the C_{1q} functions, which yield only dipoles. In other words, no superposition can generate the field pattern of a quadrupole moment, for example.

Where this dipole points, and how its orientation evolves with time, however, can be complicated. For example, a superposition of $|+1\bar{\omega}, +\rangle$ and $|+1\bar{\omega}, -\rangle$ can bob up and down, just like the analogous superposition for $j = 1/2$. However, for $j = 1$ molecules additional superpositions are possible. For example, consider the combination

$$|\psi\rangle_3 = Ae^{i\omega_0 t}|+1\bar{\omega}, +\rangle + Be^{i\omega_\Delta t}|0\bar{\omega}, +\rangle + Ce^{i\omega_0 t}|-1\bar{\omega}, -\rangle,$$

where $\hbar\omega_\Delta = \Delta/2$ is a shorthand notation for half the lambda doubling energy. Let us further assume for convenience that A, B, and C are all real. Then the expectation value of the electrostatic potential is

$$_3\langle\psi|\Phi(\vec{r})|\psi\rangle_3 \quad = \quad \frac{\mu}{2}\cos 2\delta_1\left(A^2 + C^2\right)\frac{\cos\theta}{r^2}$$

$$
\begin{aligned}
+\quad & \frac{\mu}{\sqrt{2}}\cos(\delta_1+\pi/4)B\frac{\sin\theta}{r^2} \\
\times\quad & \left[A\cos((\omega_\Delta-\omega_0)t-\phi)-C\cos(-(\omega_\Delta-\omega_0)t-\phi)\right].
\end{aligned}
$$

By analogy with remarks in the previous section, this represents a dipole with a constant component along the z-axis, which depends on both the strength of the field and on $|A|^2+|C|^2$, the total population in the $\pm m$ states. It also has a component in the x-y plane, orthogonal to the field's direction. In the case where $C=0$, this component would precess around the field axis with a frequency $\omega_\Delta-\omega_0$, in a clockwise direction as viewed from the $+z$ direction. Vice-versa, if $A=0$, this component would rotate at this frequency but in a counter-clockwise direction. If both components are present and $A=C$, then the result will be, not a rotation, but an oscillation of this component from, say, $+x$ to $-x$, in much the same way that linearly polarized light in a superposition of left- and right-circularly polarized components. More generally, if $A\neq C$, then the tip of the dipole moment will trace out an elliptical path. However, in the limit of zero field, ω_0 reduces to ω_Δ and these time-dependent effects go away.

Table 2: Matrix elements of C_{1q} for a $j = 1$ molecule. To obtain the matrix elements of the electrostatic potential $\Phi(\vec{r})$, these matrix elements should be multiplied by $(-1)^q C_{k-q}(\theta\phi)\mu/r^2$, where $q = m - m'$.

	$\lvert+1\bar{\omega}+\rangle$	$\lvert+1\bar{\omega}-\rangle$	$\lvert 0\bar{\omega}+\rangle$	$\lvert 0\bar{\omega}-\rangle$	$\lvert-1\bar{\omega}+\rangle$	$\lvert-1\bar{\omega}-\rangle$
$\langle+1\bar{\omega}+\rvert$	$\frac{1}{2}\cos 2\delta_1$	$-\frac{1}{2}\sin 2\delta_1$	$-\frac{1}{2}\cos(\delta_1+\pi/4)$	$\frac{1}{2}\sin(\delta_1+\pi/4)$	0	0
$\langle+1\bar{\omega}-\rvert$	$-\frac{1}{2}\sin 2\delta_1$	$-\frac{1}{2}\cos 2\delta_1$	$\frac{1}{2}\sin(\delta_1+\pi/4)$	$\frac{1}{2}\cos(\delta_1+\pi/4)$	0	0
$\langle 0\bar{\omega}+\rvert$	$\frac{1}{2}\cos(\delta_1+\pi/4)$	$-\frac{1}{2}\sin(\delta_1+\pi/4)$	0	0	$-\frac{1}{2}\cos(-\delta_1+\pi/4)$	$\frac{1}{2}\sin(-\delta_1+\pi/4)$
$\langle 0\bar{\omega}-\rvert$	$-\frac{1}{2}\sin(\delta_1+\pi/4)$	$-\frac{1}{2}\cos(\delta_1+\pi/4)$	0	0	$\frac{1}{2}\sin(-\delta_1+\pi/4)$	$\frac{1}{2}\cos(-\delta_1+\pi/4)$
$\langle-1\bar{\omega}+\rvert$	0	0	$\frac{1}{2}\cos(-\delta_1+\pi/4)$	$-\frac{1}{2}\sin(-\delta_1+\pi/4)$	$-\frac{1}{2}\cos 2\delta_1$	$-\frac{1}{2}\sin 2\delta_1$
$\langle-1\bar{\omega}-\rvert$	0	0	$-\frac{1}{2}\sin(-\delta_1+\pi/4)$	$-\frac{1}{2}\cos(-\delta_1+\pi/4)$	$-\frac{1}{2}\sin 2\delta_1$	$\frac{1}{2}\cos 2\delta_1$

5 Interaction of dipoles

Having thus carefully treated individual dipoles and their quantum mechanical matrix elements, we are now in a position to do the same for the dipole-dipole interaction between two molecules. This interaction depends on the orientation of each dipole, $\vec{\mu}_1$ and $\vec{\mu}_2$; and on their relative location, $\vec{R}$. This interaction has the form (Appendix A)

$$
\begin{aligned}
V_d(\vec{r}) &= \frac{\vec{\mu}_1 \cdot \vec{\mu}_2 - 3(\vec{\mu}_1 \cdot \hat{r})(\vec{\mu}_2 \cdot \hat{r})}{R^3} \\
&= -\frac{\sqrt{6}\mu^2}{R^3} \sum_q (-1)^q \left[\mu_1 \otimes \mu_2\right]_{2q} C_{2-q}(\theta\phi).
\end{aligned}
\tag{26}
$$

In going from the first line to the second, we assume that both molecules have the same size dipole moment μ, and that the intermolecular axis makes an angle θ with respect to the laboratory z axis, so that $\vec{R} = (R, \theta, \phi)$. The angles θ and ϕ thus stand for something slightly different than in the previous section. The third line in (26) rewrites the interaction in a compact tensor notation that is useful for the calculations we are about to do. Here

$$
[\mu_1 \otimes \mu_2]_{2q} = \sqrt{5} \sum_{q_1 q_2} (-1)^q \begin{pmatrix} 2 & 1 & 1 \\ q & -q_1 & -q_2 \end{pmatrix} C_{1q_1}(\beta_1\alpha_1) C_{1q_2}(\beta_2\alpha_2)
$$

denotes the second-rank tensor composed of the two first-rank tensors (i.e., vectors) $C_{1q_1}(\beta_1\alpha_1)$ and $C_{1q_2}(\beta_2\alpha_2)$ that give the orientation of the molecular axes [1]. Equation (26) highlights the important point that the orientations of the dipoles are intimately tied to the relative motion of the dipoles: if a molecule changes its internal state and sheds angular momentum, that angular momentum may appear in the orbital motion of the molecules around each other.

5.1 Potential matrix elements

Equation (26) is a perfectly reasonable way of writing the classical dipole-dipole interaction. Quantum mechanically, however, we are interested in molecules that are in particular quantum states $|jm\bar{\omega}, \epsilon\rangle$, rather than molecules whose dipoles point in particular directions (α, β). We must therefore construct matrix elements of the interaction potential (26) in the basis we have described in Sec. 3.3.

Writing the interaction in the form above has the advantage that each term in the sum factors into three pieces: one depending on the coordinates of molecule 1, another depending on the coordinates of molecule 2, and a third depending on the relative coordinates (θ, ϕ). This makes it easier to evaluate the Hamiltonian in a given basis. For two molecules we consider the basis functions

$$
\langle \alpha_1\beta_1 | jm_1\bar{\omega}, \epsilon_1 \rangle \langle \alpha_2\beta_2 | jm_2\bar{\omega}, \epsilon_2 \rangle,
\tag{27}
$$

as defined above. In this basis, matrix elements of the interaction become

$$
\begin{aligned}
&\langle jm_1\bar{\omega}, \epsilon_1; jm_2\bar{\omega}, \epsilon_2|V_d(\theta,\phi)|jm_1'\bar{\omega}, \epsilon_1'; jm_2'\bar{\omega}, \epsilon_2'\rangle = \\
&-\frac{\sqrt{30}\mu^2}{R^3}\begin{pmatrix} 2 & 1 & 1 \\ q & -q_1 & -q_2 \end{pmatrix} \\
&\times\langle jm_1\bar{\omega}, \epsilon_1|C_{1q_1}|jm_1'\bar{\omega}, \epsilon_1'\rangle\langle jm_2\bar{\omega}, \epsilon_2|C_{1q_2}|jm_2'\bar{\omega}, \epsilon_2'\rangle C_{2-q}(\theta,\phi)
\end{aligned}
\tag{28}
$$

where matrix elements of the form $\langle jm\bar{\omega}, \epsilon|C_{1q}|jm'\bar{\omega}, \epsilon'\rangle$ are evaluated in Eq. (22). Conservation of angular momentum projection constrains the values of the summation indices, so that $q_1 = m_1 - m_1'$, $q_2 = m_2 - m_2'$, and $q = q_1 + q_2 = (m_1 + m_2) - (m_1' + m_2')$. To make this model concrete, we report here the values of the second-rank reduced spherical harmonics [1]:

$$
\begin{aligned}
C_{20} &= \frac{1}{2}\left(3\cos^2\theta - 1\right) \\
C_{2\pm1} &= \mp\left(\frac{3}{2}\right)^{1/2}\cos\theta\sin\theta e^{\pm i\phi} \\
C_{2\pm2} &= \left(\frac{3}{8}\right)^{1/2}\sin^2\theta e^{\pm 2i\phi}.
\end{aligned}
$$

We also tabulate the relevant 3-j symbols in Table III.

Viewed roughly as a collision process, we can think of two molecules approaching each other with angular momenta m_1 and m_2, scattering, and departing with angular momenta m_1' and m_2', in which case q is the angular momentum transferred to the relative angular momentum of the pair of molecules. Remarkably, apart from a numerical factor that can be easily calculated, the part of the quantum mechanical dipole-dipole interaction corresponding to angular momentum transfer q has an angular dependence given simply by the multipole term C_{2-q}.

Suppose that the molecules, when far apart, are in the well-defined states (27). Then the diagonal matrix element of the dipole-dipole potential evaluates to

$$
\left(\mu\frac{m_1\epsilon_1\bar{\omega}}{j(j+1)}\cos 2\delta_{m_1}\right)\left(\mu\frac{m_2\epsilon_2\bar{\omega}}{j(j+1)}\cos 2\delta_{m_2}\right)\frac{(1 - 3\cos^2\theta)}{R^3}.
\tag{29}
$$

This has exactly the form of the interaction for classical, polarized dipoles, as in Eq. (3). The difference is that each dipole μ is replaced by a quantum-corrected version (in large parentheses). It is no coincidence that this is the same quantum-corrected dipole moment that appeared in the expression (23) for the field due to a single dipole. When both dipoles are aligned with the field, we have $m_1\epsilon_1 > 0$ and $m_2\epsilon_2 > 0$ (e.g., both molecules are of type $|a\rangle$), and the interaction has the angular dependence $\propto (1 - 3\cos^2\theta)$. On the other hand, when one dipole is aligned with the field and the other is against (e.g., one molecule is of type $|a\rangle$ and the other is of type $|c\rangle$), then the opposite sign occurs – just as we would expect from classical intuition.

More generally, at finite electric field, or at finite values of R, the molecules do *not* remain in the separated-molecule eigenstates (27), since they exert torques

Table 3: The 3-j symbols needed to construct the matrix elements in (28). Note that these symbols remain invariant under interchanging the indices q_1 and q_2, as well as under simultaneously changing the signs of $q-1$, q_2, and q [1].

q	q_1	q_2	$\begin{pmatrix} 2 & 1 & 1 \\ q & -q_1 & -q_2 \end{pmatrix}$
0	0	0	$\sqrt{2/15}$
0	1	-1	$1/\sqrt{30}$
1	1	0	$-1/\sqrt{10}$
2	1	1	$1/\sqrt{5}$

on one another. The interaction among several different internal molecular states makes the scattering of two molecules a "multichannel problem," the formulation and solution of which is described in Chapters XXX. However, a good way to visualize the action of the dipole-dipole potential on the molecules is to construct an adiabatic surface. To do so, we diagonalize the interaction at a fixed value of $\vec{R}$, the relative location of the two molecules.

Before doing this, we must consider the quantum statistics of the molecules. If the two molecules under consideration are identical bosons or identical fermions, then the total two-molecule wave function must account for this fact. This total wave function is

$$\langle \alpha_1\beta_1\gamma_1|jm_1\bar{\omega}\epsilon_1\rangle\langle\alpha_2\beta_2\gamma_2\rangle|jm_2\bar{\omega}\epsilon_2\rangle F_{j\bar{\omega};m_1\epsilon_1 m_2\epsilon_2}(R,\theta,\phi).$$

This wave function is either symmetric or antisymmetric under the exchange of the two particles, which is accomplished by swapping the internal states of the molecules, while simultaneously exchanging their center-or-mass coordinates, i.e., by mapping $\vec{R}$ to $-\vec{R}$:

$$\begin{aligned} (\alpha_1\beta_1) &\leftrightarrow (\alpha_2\beta_2) \\ R &\rightarrow R \\ \theta &\rightarrow \pi - \theta \\ \phi &\rightarrow \pi + \phi. \end{aligned} \tag{30}$$

For the molecule's internal coordinates, a wave function with definite exchange symmetry is given by

$$\begin{aligned} &\langle\alpha_1\beta_1\gamma_1|jm_1\bar{\omega}\epsilon_1\rangle\langle\alpha_2\beta_2\gamma_2\rangle|jm_2\bar{\omega}\epsilon_2\rangle_s \\ &= \frac{1}{\sqrt{2(1+\delta_{m_1 m_2}\delta_{\epsilon_1\epsilon_2})}} \\ &\times \left[\langle\alpha_1\beta_1\gamma_1|jm_1\omega\epsilon_1\rangle\langle\alpha_2\beta_2\gamma_2|jm_2\omega\epsilon_2\rangle + s\langle\alpha_2\beta_2\gamma_2|jm_1\omega\epsilon_1\rangle\langle\alpha_1\beta_1\gamma_1|jm_2\omega\epsilon_2\rangle\right]. \end{aligned} \tag{31}$$

The new index $s = \pm 1$ denotes whether the combination (31) is even or odd under the interchange. If $s = +1$, then F must be symmetric under the trans-

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formation $\vec{R} \to -\vec{R}$ for bosons, and odd under this transformation for identical fermions. If $s = -1$, the reverse must hold.

We now have the tools required to consider the form of the dipole-dipole interaction beyond the "pure" dipolar form (29). The details of this analysis will depend on the Schrödinger equation to be solved. In its fundamental form, the Schrödinger equation reads

$$\left(-\frac{\hbar^2}{2m_r}\nabla^2 + V_d + H_S\right)\Psi = E\Psi.$$

Here H_S stands for the threshold Hamiltonian that includes Λ-doubling and electric field interactions, and is assumed to be diagonal in the basis (31); and m_r is the reduced mass of the pair of molecules. In the usual way, we expand the total wave function ψ as

$$\Psi(R, \theta, \phi) = \frac{1}{R}\sum_{i'} F_{i'}(R, \theta, \phi)|i'\rangle,$$

where the index i stands for the collective set of quantum numbers $\{j\bar{\omega}; m_1\epsilon_1 m_2\epsilon_2 s\}$.

Inserting this expansion into the Schrödinger equation and projecting onto the ket $\langle i|$ leads to the following set of coupled equations:

$$-\frac{\hbar^2}{2m_r}\left[\frac{\partial^2}{\partial R^2} + \frac{1}{R^2 \sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{R^2 \sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]F_i$$
$$+ \sum_{i'}\langle i|V_d|i'\rangle F_{i'} + \langle i|H_S|i\rangle F_i = EF_i.$$

If we keep N channels i, then this represents a set of N coupled differential equations. We can, in principle, solve these subject to physical boundary conditions for any bound or scattering problem at hand. For visualization, however, we will find it convenient to reduce these equations to fewer than three independent variables. We carry out this task in the following subsections.

5.2 Adiabatic potential energy surfaces in two dimensions

Applying an electric field in the $\hat{z}$ direction establishes $\hat{z}$ as an axis of cylindrical symmetry for the two-body interaction. The angle ϕ determines the relative orientation of the two molecules about this axis, thus the interaction cannot depend on this angle. To handle this, we include an additional factor in our basis set,

$$|m_l\rangle = \frac{1}{\sqrt{2\pi}}\exp(im_l\phi).$$

We then expand the total wave function as

$$\Psi^{M_{tot}}(R, \theta, \phi) = \frac{1}{R}\sum_{i'm_l'} F_{i'm_l'}(R, \theta)|m_l'\rangle|i'\rangle.$$

In each term of this expression the quantum numbers must satisfy the conservation requirement for fixed total angular momentum projection, $M_{tot} = m_1 + m_2 + m_l$. In addition, applying exchange symmetry to each term requires that $F_{i,m_l}(R, \pi - \theta) = s(-1)^{m_l} F_{i,m_l}(R, \theta)$ for bosons, and $s(-1)^{m_l+1} F_{i,m_l}(R, \theta)$ for fermions.

Inserting this expansion into the Schrödinger equation yields a slightly different set of coupled equations:

$$-\frac{\hbar^2}{2m_r} \left[\frac{\partial^2}{\partial R^2} + \frac{1}{R^2 \sin^2 \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) \right] F_{i,m_l} \tag{32}$$

$$+ \frac{\hbar^2 m_l^2}{2m_r R^2 \sin^2 \theta} F_{im_l} + \sum_{i'} \langle i | V_d^{2D} | i' \rangle F_{i'm_l'} + \langle i | H_S | i \rangle F_{im_l} = E F_{im_l}.$$

This substitution has the effect of replacing the differential form of the azimuthal kinetic energy, $\propto \partial^2/\partial\phi^2$, by an effective centrifugal potential $\propto m_l^2 / R^2 \sin^2 \theta$. In addition, the matrix elements of the dipolar potential V_d^{2D} are slightly different from those of V_d. Recall that the θ dependent part of the matrix element (28) is proportional to $C_{2-q}(\theta, \phi)$, which we will write explicitly as

$$C_{2-q}(\theta, \phi) \equiv C_{2-q}(\theta) \exp(-iq\phi).$$

This equation explicitly defines a new function $C_{2-q}(\theta)$ that is a function of θ alone, and that is proportional to an associated Legendre polynomial. The matrix element of the potential now includes the following integral:

$$\begin{aligned} \langle m_l | C_{2-q} | m_l' \rangle &= \int d\phi \frac{1}{\sqrt{2\pi}} e^{-im_l\phi} C_{2-q}(\theta) e^{-iq\phi} \frac{1}{\sqrt{2\pi}} e^{im_l'\phi} \\ &= \frac{C_{2-q}(\theta)}{2\pi} \int d\phi e^{i(M_{tot}' - M_{tot})\phi} \\ &= \delta_{M_{tot} M_{tot}'} C_{2-q}(\theta), \end{aligned}$$

which establishes the conservation of the projection of total angular momentum by the dipole-dipole interaction. Therefore, matrix elements of V_d^{2D} in this representation are identical to those in of V_d in Eq. (28) *except* that the factor $\exp(-iq\phi)$ is replaced by $\delta_{M_{tot} M_{tot}'}$.

With these matrix elements in hand, we can construct solutions to the coupled differential equations (32). However, to understand the character of the potential surface, it is useful to construct adiabatic potential energy surfaces. This means that, for a fixed relative position of the molecules (R, θ), we find the energy spectrum of (32) by diagonalizing the Hamiltonian $V_c^{2D} + V_d^{2D} + H_S$, where V_c^{2D} is a shorthand notation for the centrifugal potential discussed above. This approximation is common throughout atomic and molecular physics, and amounts to defining a single surface that comes as close as possible to representing what is, ultimately, multichannel dynamics.

5.3   Example: $j = 1/2$ molecules

Analytic results for the adiabatic surfaces are rather difficult to obtain. Consider the simplest realization of our model, a molecule with spin $j = 1/2$. In this case each molecule has four internal states (two values of m and two values of ϵ), so that the two-molecule basis comprises sixteen elements. Dividing these according to exchange symmetry of the molecules' internal coordinates, there are ten channels within the manifold of $s = +1$ channels, and six within the $s = -1$ manifold. These are the cases we will discuss in the following, although the same qualitative features also appear in higher-j molecules.

As the simplest illustration of the influence of internal structure on the dipolar interaction, we will focus on the lowest-energy adiabatic surface, and show how it differs from the "pure dipolar" result (29) as the molecules approach one another. The physics underlying this difference arises from the fact that the dipole-dipole interaction becomes stronger as the molecules get closer together, and at some point this interaction is stronger than the action of the external field that holds their orientation fixed in the lab. The intermolecular distance at which this happens can be approximately calculated by setting the two interactions equal, $\mu^2/R_0^3 = \sqrt{(\mu\mathcal{E})^2 + (\Delta/2)^2}$, yielding a characteristic distance

$$R_0 = \left(\frac{\mu^2}{\sqrt{(\mu\mathcal{E})^2 + (\Delta/2)^2}} \right)^{1/3}.$$

When $R \gg R_0$, the electric field interaction is dominant, the dipoles are aligned, and the interaction is given by Eq. (29). When R becomes comparable to, or less than, R_0, then the dipoles tend to align in a head-to-tail orientation to minimize their energy, regardless of their relative location.

Before proceeding, it is instructive to point out how large the scale R_0 can be for realistic molecules. For the OH molecule considered above, with $\mu = 1.7$ Debye and $\Delta = 0.06$ cm^{-1}, the molecule can be polarized in a field of $\mathcal{E} \approx 1600$ V/cm. At this field, the characteristic radius is approximately $R_0 \approx 120\ a_0$ (where $a_0 = 0.053$ nm is the Bohr radius), far larger than the scale of the molecules themselves. Therefore, while the dipole-dipole interaction is by far the largest interaction energy at large R, over a significant range of this potential does not take the usual dipolar form. To take an even more extreme case, the molecule NiH has a ground state of $^2\Delta$ symmetry with $j = 5/2$ [2]. Because it is a Δ, rather than a Π, state, its Λ doublet is far smaller, probably on the order of $\sim 10^{-5}$ cm^{-1}. This translates into a critical field of $\mathcal{E} \approx 0.5$ V/cm, and a characteristic radius at this field $R_0 \approx 2000\ a_0 \approx 0.09\ \mu$m. This length is approaching a non-negligible fraction of the interparticle distance in a Bose-Einstein condensed sample of such molecules (assuming a density of 10^{14} cm^{-3}, this spacing is of order 0.2 μm). Deviations from the simple dipolar behavior may thus influence the macroscopic properties of a quantum degenerate dipolar gas.

As an example, we present in Figure 2 sections of the lowest-energy adiabatic potential energy surfaces for a ficticious $j = 1/2$ molecule whose mass, dipole

moment, and Λ doublet are equal to those of OH. These were calculated in a strong-field limit with $\mathcal{E} = 10^4$ V/cm. Each row corresponds to a particular intermolecular separation, which is compared to the characteristic radius R_0. However, as noted above, there are two possible ways for the molecule to have its lowest energy, as illustrated by parts (a) and (b) of Figure 1. Interestingly, it turns out that these give rise to rather different adiabatic surfaces. To illustrate this, we show in the left column of Figure 2 the surface for a pair of type $|a\rangle$ molecules, which corresponds at infinitely large R to the channel $|\frac{1}{2}+, \frac{1}{2}+; s = 1\rangle$; and in the right column we show combinations of one type $|a\rangle$ and one type $|b\rangle$ molecule. In the latter case, there are two possible symmetries corresponding to $s = \pm 1$, both of which are shown. Finally, for comparison, the unperturbed "pure dipole" result is shown in all panels as a dotted line.

Consider first two molecules of type $|a\rangle$ (left column of Fig.2). For large distances $R > R_0$ (top panel), the adiabatic potential deviates only slightly from the pure-state result, reducing the repulsion at $\theta = \pi/2$. When R approaches the characteristic radius R_0 (middle panel), the effect of mixing in the higher-energy channels becomes apparent. Finally, when $R < R_0$ (lower panel), the mixing is even more significant. In this case the dipole-dipole interaction is the dominant energy, with the threshold energies serving as a small perturbation. As a consequence, the quantum numbers $|\frac{1}{2}+, \frac{1}{2}+; s = 1\rangle$ can no longer identify the channel. It is beyond the scope of this chapter to discuss the corresponding eigenstates in detail. Nevertheless, we find that for $R < R_0$ the channel $|aa\rangle$ (repulsive at $\theta = \pi/2$) is strongly mixed with the channel $|ac\rangle$ (attractive at $\theta = \pi/2$). The combination is just sufficient that the two channels nearly cancel out one another's θ-dependence. At the ends of the range, however, the adiabatic curve is contaminated by a small amount of channels containing centrifugal energy $\propto 1/\sin^2 \theta$.

The right column of Figure 2 shows adiabatic curves for the mixed channels, one molecule of type $|a\rangle$ and one of type $|b\rangle$. In this case there are two possible signs of s; These are distinguished by using solid lines for channel $|\frac{1}{2}+, -\frac{1}{2}-; s = 1\rangle$; and dashed lines for channel $|\frac{1}{2}+, -\frac{1}{2}-; s = -1\rangle$. Strikingly, these surfaces are different both from one another, and from the surfaces in the left column of the figure. Ultimately this arises from different kinds of channel couplings in the potentials (28). Note that, while type $|a\rangle$ and type $|b\rangle$ molecules are identical in their interaction energy with the electric field, they still represent different angular momentum states. Nevertheless, molecules in these channels still closely reflect the pure dipolar potential at large R, and become nearly θ-independent for small R.

A further important point is that the potentials described here represent large energies as compared to the mK or μK translational kinetic energies of cold molecules, and will therefore significantly influence their dynamics. Further, the potentials depend strongly on the value of the electric field of the environment, both through the direct effect of polarization on the magnitude of the dipole moments, and through the influence of the field on the characteristic radius R_0. It is this sensitivity to field that opens the possibility of control over interactions in an ultracold dipolar gas.

Figure 2: Angular dependence of adiabatic potential energies for various combinations of molecules at different interparticle spacings R, which are indicted on the right side. Dotted lines: diagonal matrix element of the interaction, assuming both molecules remain strongly aligned with the electric field. Solid and dashed lines: adiabatic surfaces. These surfaces are based on the $j = 1/2$ model discussed in the text, using $\mu = 1.68$ Debye, $\Delta = 0.056$ cm^{-1}, $m_r = 8.5$ amu, and $\mathcal{E} = 10^4$ V/cm, yielding $R_0 \sim 70a_0$. The left hand column presents results for two molecules of type $|a\rangle$, as labeled in Fig. 1; in the right column are results for one molecule of type $|a\rangle$ and one of type $|b\rangle$, which necessitates specifying an exchange symmetry s.

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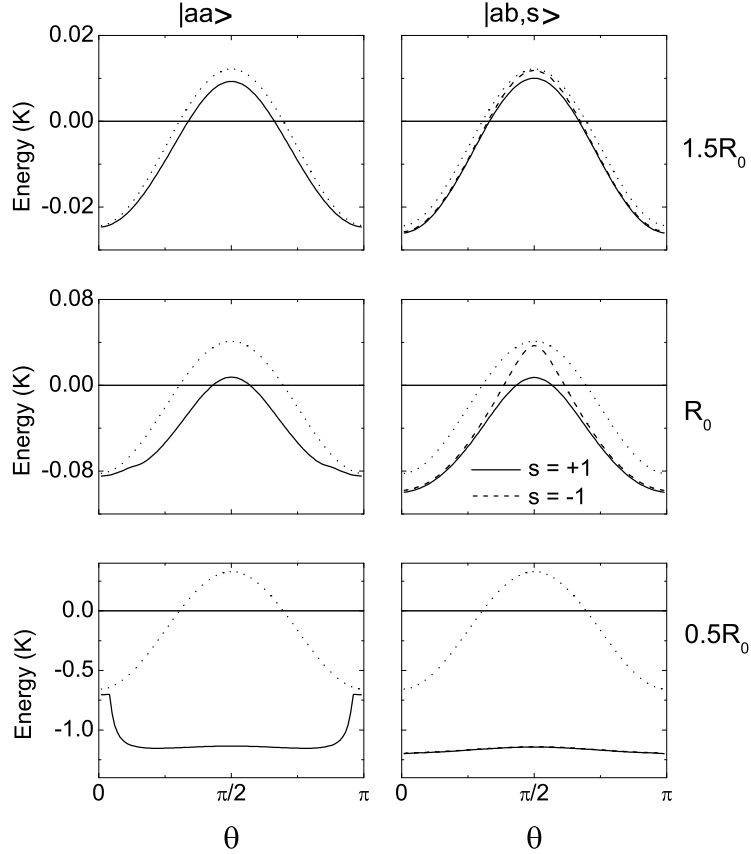
Although we have limited the discussion here to the lowest adiabatic state, interesting phenomena are also expected to arise due to avoided crossings in excited states. Notable is a collection of long-range quasi-bound states, whose intermolecular spacing is roughly centered around R_0 [7]. Such states could conceivably be used to associate pairs of molecules into well-characterized transient states, furthering the possibilities of control of molecular interactions.

5.4 Adiabatic potential energy curves in one dimension: partial waves

For many scattering applications, it is not necessarily convenient to express the dipole-dipole interaction as a surface (more properly, a set of surfaces) in the variables (R, θ, ϕ) describing the relative position and orientation of the molecules. Rather, it is useful to expand the relative angular coordinates (θ, ϕ) in a basis as well. To do this, the basis set (27) is augmented by spherical harmonics describing the relative orientation of the molecules, to become

$$\langle \alpha_1 \beta_1 \gamma_1 | j m_1 \bar{\omega} \epsilon_1 \rangle \langle \alpha_2 \beta_2 \gamma_2 | j m_2 \bar{\omega} \epsilon_2 \rangle \langle \theta \phi | l m_l \rangle,$$

with

$$\langle \theta \phi | l m_l \rangle = Y_{l m_l}(\theta \phi) = \sqrt{\frac{2l + 1}{4\pi}} C_{l m_l}(\theta \phi).$$

The total wave function is therefore described by the superposition

$$\Psi^{M_{tot}}(R, \theta, \phi) = \frac{1}{R} \sum_{i', l', m'_l} F_{i', l', m'_l} Y_{l' m'_l}(\theta \phi) | i' \rangle,$$

which represent a conventional expansion into partial waves. The wave function is, as above, restricted by conservation of angular momentum to require $M_{tot} = m_1 + m_1 + m_l$ to have a constant value. Moreover, the effect of the symmetry operation (30) on $|l m_l\rangle$ is to introduce a phase factor $(-1)^l$. Therefore, the wave function is restricted to $s(-1)^l = 1$ for bosons, and $s(-1)^l = -1$ for fermions.

The effect of this extra basis function is to replace the C_{2-q} factor in (28) by its matrix element

$$
\begin{aligned}
C_{2-q} \rightarrow \quad & \langle l m_l | C_{2-q} | l' m'_l \rangle \\
& = \sqrt{(2l+1)(2l'+1)} (-1)^{m_l} \begin{pmatrix} l & 2 & l \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l & 2 & l \\ -m_l & -q & m'_l \end{pmatrix}
\end{aligned}
\tag{33}
$$

From this expression it is seen that the angular momentum q, lost to the internal degrees of freedom of the molecules, appears as the change in their relative orbital angular momentum. From here, the effects of field dressing are exactly as treated above.

The quantum number l, as is usual in quantum mechanics when treated in spherical coordinates, represents the orbital angular momentum of the pair of

molecules about their center of mass. Following the usual treatment, this leads to a set of coupled radial Schrödinger equations for the relative motion of the molecules:

$$-\frac{\hbar^2}{2m_r}\frac{d^2 F_{ilm_l}}{dR^2} \qquad +\frac{\hbar^2 l(l+1)}{2m_r R^2}F_{ilm_l}$$
$$+\sum_{i'}\langle i|V_d^{1D}|i'\rangle F_{i'l'm_l'} + \langle i|H_S|i\rangle F_{ilm_l} = EF_{ilm_l}.$$

The second term in this expression represents a centrifugal potential $\propto 1/R^2$, which is present for all partial waves $l > 0$.

5.5   Asymptotic form of the interaction

Casting the Schrödinger equation as an expansion in partial waves, and the interaction as a set of curves in R, rather than as a surface in (R, θ, ϕ), allows us to explore more readily the long-range behavior of the dipole-dipole interaction.

The first 3-j symbol in (33) vanishes unless $l + 2 + l'$ is an odd number, meaning that even(odd) partial waves are coupled only to even(odd) partial waves. Moreover, the values of l and l' can differ by at most two. Thus the dipolar interaction can change the orbital angular momentum state from $l = 2$ to $l' = 4$, for instance, but not to $l' = 6$. Finally, the interaction vanishes altogether for $l = l' = 0$, meaning that the dipole-dipole interaction nominally vanishes in the s-wave channel.

Since all other channels have higher energy, due to their centrifugal potentials, it appears that the lowest adiabatic curve is trivially equal to zero. This is not the case, however, since the s-wave channel is coupled to a nearby d-wave channel with $l = 2$. Ignoring for the moment higher partial waves, the Hamiltonian corresponding to a particular channel i at long range has the form

$$\begin{pmatrix} 0 & A_{02}/R^3 \\ A_{20}/R^3 & 3\hbar^2/m_r R^2 + A_{22}/R^3 \end{pmatrix}.$$

Here $A_{02} = A_{20}$ and A_{22} are coupling coefficients that follow from the expressions derived above. Note that all these coefficients are functions of the electric field $\mathcal{E}$. Now, the comparison of dipolar and centrifugal energies defines another typical length scale for the interaction, namely, the one where $\mu^2/R^3 = \hbar^2/m_r R^2$, defining a "dipole radius" $R_D = \mu^2 m_r/\hbar^2$. (More properly, one could define an electric-field-dependent radius by substituting A_{02} for μ^2). For OH, this length is $\sim 6800\ a_0$, while for NiH it is $\sim 9000\ a_0$.

When the molecules are far apart, $R > R_D$, the dipolar interaction is a perturbation. The size of this perturbation on the s-wave interaction is found through second-order perturbation theory to be

$$\frac{(A_{02}/R^3)^2}{3\hbar^2/m_r R^2} \sim \left(\frac{A_{02}^2 m_r}{3\hbar^2}\right)\frac{1}{R^4}.$$

Therefore, at very large intermolecular distances, the effective potential, as described by the lowest adiabatic curve, carries a $1/R^4$ dependence on R, rather than the nominal $1/R^3$ dependence. At closer range, when $R < R_D$, the $1/R^3$ terms dominate the $1/R^2$ centrifugal interaction, and the potential reduces again to the expected $1/R^3$ dependence on R.

6   Acknowledgements

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