

Dipole Interaction of the Rigid Rotor

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In this problem, we derive the permanent and induced dipole moments and the perturbative Stark shift of a rigid rotor molecule with a fixed (molecule-frame) electric dipole moment \vec{d}_{mol} and moment of inertia I .

1 Rigid Rotor

First, let's review the solution to the rigid rotor problem (For more details see, e.g. Brown and Carrington chapter 6.8.1 [1] and Townes and Schawlow chapter 1.1 [5]). Consider the rigid rotor illustrated in Fig. 1, which consists of a pair of masses M_1 and M_2 separated by a fixed distance R . In the center-of-mass frame, this system reduces to a single mass $\mu = \frac{M_1 M_2}{M_1 + M_2}$ constrained to the surface of a sphere of radius R . The energy is just the kinetic energy of a system with angular degrees of freedom (θ, ϕ) , which is given by

$$H_{\text{rot}} = \vec{J}^2 / 2I, \quad (1)$$

where \vec{J} is the angular momentum operator, and $I = \mu R^2$ is the moment of inertia. The solutions to the time-independent Schrödinger equation $H_{\text{rot}} \psi(\theta, \phi) = E \psi(\theta, \phi)$ are the spherical harmonics

$$\psi(\theta, \phi) = Y_J^m(\theta, \phi), \quad (2)$$

with eigenenergies

$$E_{J,m} = \frac{\hbar^2}{2I} J(J+1). \quad (3)$$

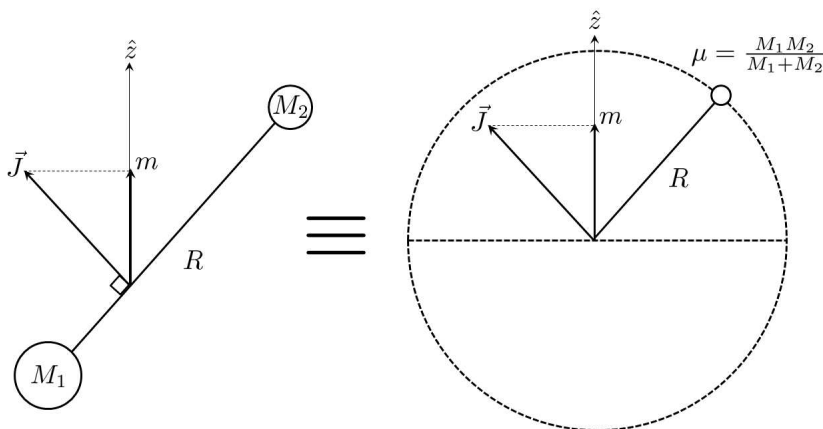


Figure 1: Rigid rotor. In its center-of-mass frame, the dumbbell model on the left is mathematically equivalent to a single particle of reduced mass μ constrained to the surface of a sphere of radius R , as depicted on the right.

In the frame of reference that rotates with the molecule, the rigid rotor dipole moment \vec{d}_{mol} is equal to $\Delta q \vec{R}$, where Δq is the absolute value of the charge excess per atom and depends on the internal structure of the atoms and on the properties of the molecular bond.

2 Permanent EDM

Problem: Find the expectation value $\langle \vec{d} \rangle$ of the electric dipole operator \vec{d} in an energy eigenstate $|J, m\rangle$.

Solution: The dipole operator changes the parity of the state it acts upon, so it cannot connect two parity eigenstates with the same parity. Specifically, it cannot connect $|J, m\rangle$ to itself. Therefore, the expectation value of the electric dipole moment is zero in the lab frame, even though the molecule may have a nonzero dipole moment \vec{d}_{mol} in the frame of reference that rotates with the molecule. Note that this also means that the linear Stark shift $E_{\text{St}}^{(1)} = \langle \vec{d} \rangle \cdot \vec{\mathcal{E}}$ vanishes.

To see explicitly that a permanent zero-field electric dipole moment (EDM) is forbidden by parity, we use the transformation properties of $|J, m\rangle$ and \vec{d} under the parity operator P :

$$P\vec{d}P^\dagger = qP\vec{r}P^\dagger = -q\vec{r} = -\vec{d}, \text{ and} \quad (4)$$

$$P|J, m\rangle = (-1)^J |J, m\rangle. \quad (5)$$

In Eq. (4), we have used the fact that the dipole operator is equal to the charge q times the displacement operator \vec{r} , and the displacement transforms into its opposite under parity. Equation (5) describes the parity properties of the spherical harmonics (see, e.g. Merzbacher chapter 11.4 [4]).

Now, with malice of forethought, we calculate the negative expectation value of the dipole operator:

$$-\langle J, m | \vec{d} | J, m \rangle = \langle J, m | P^\dagger \vec{d} P | J, m \rangle \quad (6)$$

$$= \langle J, m | (-1)^J \vec{d} (-1)^J | J, m \rangle = [(-1)^{2J}] \langle J, m | \vec{d} | J, m \rangle \quad (7)$$

$$= + \langle J, m | \vec{d} | J, m \rangle \quad (8)$$

$$= 0. \quad (9)$$

In Eq. (6), we have used Eq. (4) and the hermicity of the parity operator, and in Eq. (7) we have substituted Eq. (5) for the parity operator acting on the spherical harmonics.

This proof can also be performed in position space using integrals over the spherical harmonics. See Budker, Kimball, and DeMille chapter 7.6 [2].

Note that this proof works if you substitute any eigenstate of parity for $|J, m\rangle$. In the absence of applied fields that fix a preferred direction, the Hamiltonian of a system commutes with P , so the energy eigenstates can always be written as eigenstates of parity. Thus, as long as the Hamiltonian has no degenerate eigenstates of opposite parity, *there are no permanent EDMs*.

3 Dipole matrix elements

Problem: Find a general expression for the off-diagonal matrix elements of d_z .

Solution: We can express the dipole matrix elements in terms of integrals over products of spherical harmonics:

$$\langle J', m' | \vec{d} \cdot \hat{z} | J, m \rangle = \langle J', m' | d_{\text{mol}} \cos \theta | J, m \rangle \quad (10)$$

$$= d_{\text{mol}} \int d\Omega [Y_{J'}^{m'}(\theta, \phi)]^* \cos \theta Y_J^m(\theta, \phi) \quad (11)$$

$$= d_{\text{mol}} \sqrt{\frac{4\pi}{3}} \int d\Omega [Y_{J'}^{m'}(\theta, \phi)]^* Y_1^0(\theta, \phi) Y_J^m(\theta, \phi) \quad (12)$$

where d_{mol} is the molecule-frame EDM, θ is the angle between the z-axis and the dipole moment, and ϕ is the azimuthal angle about the z-axis. In Eq. (12), we have used the formula $Y_1^0(\theta, \phi) = \sqrt{3/4\pi} \cos \theta$ to write the angular dependence of the dipole operator as a spherical harmonic.

To solve this integral, we introduce a useful identity (from Merzbacher chapter 17.6 [4]) that turns integrals over products of three spherical harmonics into Clebsch-Gordan coefficients:

$$\int d\Omega [Y_{J_3}^{m_3}(\theta, \phi)]^* Y_{J_1}^{m_1}(\theta, \phi) Y_{J_2}^{m_2}(\theta, \phi) = \sqrt{\frac{(2J_1+1)(2J_2+1)}{4\pi(2J_3+3)}} \times \langle J_2 0; J_1 0 | J_3 0 \rangle \langle J_2 m_2; J_1 m_1 | J_3 m_3 \rangle. \quad (13)$$

Substituting Eq. (12) into Eq. (13), we obtain:

$$\langle J', m' | \vec{d} \cdot \hat{z} | J, m \rangle = d_{\text{mol}} \left(\frac{2J+1}{2J'+1} \right)^{\frac{1}{2}} \langle J 0; 1 0 | J' 0 \rangle \langle J m; 1 0 | J' m' \rangle. \quad (14)$$

Now we can use the angular momentum conservation properties of the Clebsch-Gordan coefficients to constrain the possible values of J' and m' . Note that the final Clebsch-Gordan coefficient in Eq. (13) vanishes unless the z-components of the angular momenta satisfy $m_1 + m_2 = m_3$ and the total angular momenta satisfy the triangle condition $|J_3 - J_2| \leq J_1$. Since $m_1 = 0$ and $J_1 = 1$, we obtain the usual dipole selection rules $m' = m$, and $J' = J \pm 1$. (For the total angular momentum selection rule, the triangle condition tells us that J and J' differ by *at most* 1, but from Section 2, we know that the matrix element vanishes when they differ by 0; therefore, J and J' must differ by *exactly* 1.)

Thus we can write the nonvanishing matrix elements as:

$$\langle J' = J \pm 1, m' = m | \vec{d} \cdot \hat{z} | J, m \rangle = d_{\text{mol}} \left(\frac{2J+1}{2(J \pm 1) + 1} \right)^{\frac{1}{2}} \langle J 0; 1 0 | (J \pm 1) 0 \rangle \langle J m; 1 0 | (J \pm 1) m \rangle. \quad (15)$$

Next, we can use Mathematica (or the recursion relations, if you're bolder than I) to calculate the Clebsch-Gordan coefficients for the two cases $J' = J + 1$ and $J' = J - 1$. After just a line or so of algebra, we obtain the solution:

$$\langle J', m' | \vec{d} \cdot \hat{z} | J, m \rangle = d_{\text{mol}} \times \begin{cases} \left[\frac{(J-m+1)(J+m+1)}{(2J+3)(2J+1)} \right]^{\frac{1}{2}}, & \text{if } J' = J + 1 \text{ and } m' = m. \\ \left[\frac{(J-m)(J+m)}{(2J-1)(2J+1)} \right]^{\frac{1}{2}}, & \text{if } J' = J - 1 \text{ and } m' = m. \\ 0, & \text{otherwise.} \end{cases} \quad (16)$$

Dave points out that instead of looking up the slightly obscure identity in Eq. (13), it is possible to derive this result using the Wigner-Eckart theorem. I will not perform this calculation here, but essentially, one would proceed by writing down the Wigner-Eckart theorem for the matrix element between $|J', m'\rangle$ and $|J, m\rangle$ (noting that $\cos \theta$ is proportional to T_1^0), and then eliminate the reduced matrix element by solving for it in terms of the dipole matrix element between $|J', 0\rangle$ and $|J, 0\rangle$, which is an integral over spherical harmonics that can be performed in Mathematica. In the end, all unknown constants of proportionality cancel, and one is left with some Clebsch-Gordan coefficients to calculate, as above.

4 Quadratic Stark shifts

Problem: Use the solution for the dipole matrix elements from Section 3 to calculate Stark shifts of the rotational levels in an electric field $\vec{\mathcal{E}} = \mathcal{E} \hat{z}$ to lowest non-vanishing order in perturbation theory.

Solution: The Hamiltonian for the Stark shift is

$$H_{\text{St}} = -\vec{d} \cdot \vec{\mathcal{E}} = -\mathcal{E} \vec{d} \cdot \hat{z} = -\mathcal{E} d_{\text{mol}} \cos \theta. \quad (17)$$

In the perturbative limit we assume that the dipole interaction is much smaller than the rigid rotor energy level splitting, i.e. $\mathcal{E} d_{\text{mol}} \ll \hbar^2/2I$.

The first-order Stark shift is $E_{J,m}^{(1)} = \langle H_{\text{St}} \rangle = -\langle \vec{d} \rangle \cdot \vec{\mathcal{E}}$, which we know vanishes from Section 2.

We next examine the quadratic Stark shift. From non-degenerate second-order perturbation theory,¹ we have (see, e.g. Griffiths chapter 6.1.3 [3]):

$$E_{J,m}^{(2)} = \sum_{J'=J\pm 1} \frac{|\langle J', m | H_{\text{St}} | J, m \rangle|^2}{E_{J,m} - E_{J',m}}, \quad (18)$$

where I have excluded all terms in the sum ($J' \neq J \pm 1$, $m' \neq m$) that were found to vanish in Section 3. We now explicitly substitute the rigid rotor energies from Eq. (3) and write out $\langle J', m | H_{\text{St}} | J, m \rangle$ in terms of dipole matrix elements:

$$E_{J,m}^{(2)} = \frac{\mathcal{E}^2 d_{\text{mol}}^2}{\hbar^2/2I} \sum_{J'=J\pm 1} \frac{|\langle J', m | \cos \theta | J, m \rangle|^2}{J(J+1) - J'(J'-1)}. \quad (19)$$

Now we can substitute in the formula for the matrix elements calculated in Eq. (16), perform the sum over $J' = J \pm 1$, and after a few lines of algebra, we obtain:

$$E_{J,m}^{(2)} = \frac{\mathcal{E}^2 d_{\text{mol}}^2}{\hbar^2/2I} \times \begin{cases} -\frac{1}{6}, & \text{if } J = 0. \\ \frac{1}{2} \left[\frac{(J-m)(J+m)}{J(2J-1)(2J+1)} - \frac{(J-m+1)(J+m+1)}{(J+1)(2J+1)(2J+3)} \right], & \text{if } J \geq 1. \end{cases} \quad (20)$$

(This result agrees with Eq. 10.8 and 10.9 in [5] for the Stark shift of a linear molecule.)

The quadratically Stark-shifted energy levels are plotted in Fig. 2. Let's attempt a physical interpretation of a few aspects of this figure and the formulae on which it is based.

1. The Stark shift is symmetric in m (Notice that changing every instance of m to $-m$ leaves the formula unchanged). This makes physical sense because parity symmetry dictates that it shouldn't matter whether the wavefunction is circulating clockwise or counter-clockwise with respect to the direction of the electric field.
2. The magnitude of the Stark shift decreases for increasing J because there are more powers of J in the denominator than in the numerator of Eq. (20). The physical cause of this diminished perturbation is that as J increases, the rigid rotor level spacing also increases (in proportion to J), and mixing with adjacent J levels is therefore suppressed by the energy denominator in Eq. (18).
3. For the extremal values of m , given by $|m| = J$, the first (positive) term in Eq. (20) vanishes, so that the quadratic Stark shift is always negative. This happens because the dipole interaction causes adjacent energy levels to mix and repel, and the state $|J, \pm J\rangle$ can only mix with the energy level above it, $|J+1, \pm J\rangle$; the $J-1$ level has no $m = J$ sublevel with which the $|J, \pm J\rangle$ state can interact under dipole selection rules.
4. For a given rotational level, the quadratic Stark shift decreases monotonically with $|m|$; some examination of Eq. (20) reveals that the second (negative) term gradually wins out over the first (positive) term as $|m|$ approaches J . I find this behavior a bit tricky to explain from a physical perspective, but I'll make two attempts: one taking the classical point of view and one using quantum mechanics.

In the classical picture, this pattern can be understood by imagining a dipole with a given angular momentum \vec{J} whose axis of rotation points at an angle θ relative to the external field $\vec{\mathcal{E}}$. As θ approaches 0 or π (equivalent to m approaching $\pm J$), the dipole becomes oriented more and more orthogonal to the field. Therefore, the torque $|\vec{d} \times \vec{\mathcal{E}}| = d \cdot \mathcal{E} \sin(\theta + \pi/2)$, which tends to align the dipole and lower its energy, becomes stronger. Thus molecules with large values of $|m|$ tend to experience a negative Stark shift. Conversely, as θ approaches $\pi/2$, the torque that tends to align the dipole vanishes on average, and the dipole spins so that it is alternately aligned and anti-aligned with the applied field. As the spinning dipole approaches alignment with the applied field, the torque from the field accelerates its rotation so that the dipole's maximum angular velocity occurs when it is aligned with

¹Even though rigid rotor eigenstates with the same J are degenerate, we can use non-degenerate perturbation theory because as shown in Section 3, the dipole matrix elements only connect states of different J .

Rigid Rotor Energy Levels In the Presence of a Quadratic Stark Shift

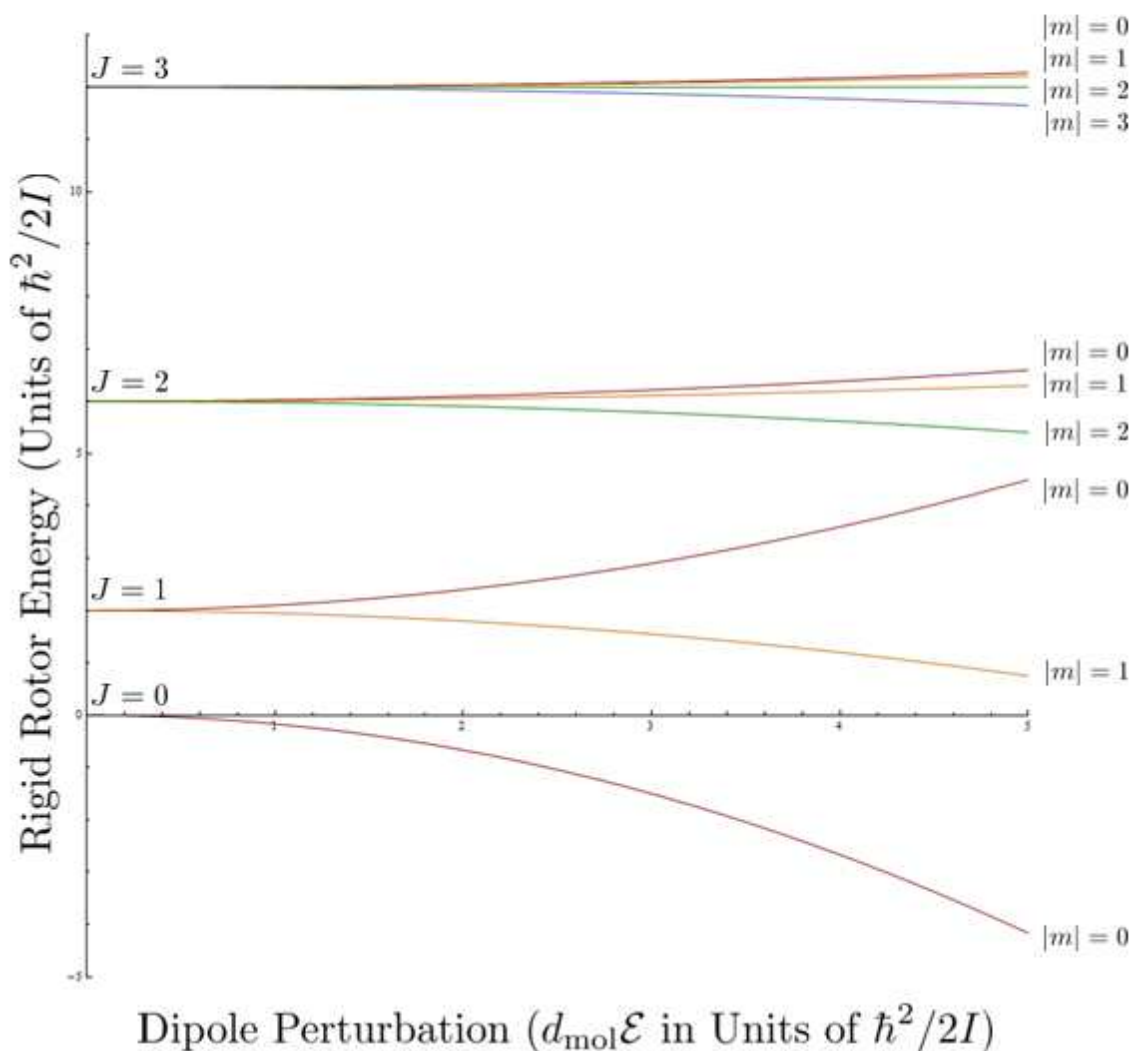


Figure 2: Energy levels of a rigid rotor molecule with dipole moment d_{mol} in an applied electric field \mathcal{E} . The quadratic Stark shifts are given as a function of electric field in units of rotational constant $\hbar^2/2I$ divided by d_{mol} . Technically, these perturbative results are valid only at \mathcal{E} values much less than 1 on the x-axis, but the Stark shifts are shown here out to large values of \mathcal{E} so that the shifts at higher J are visible.

$\vec{\mathcal{E}}$. For similar reasons, the minimum angular velocity occurs when the dipole is anti-aligned with the applied field. Thus a spinning molecule with small m spends more time pointing against $\vec{\mathcal{E}}$ than with it and experiences a positive Stark shift. (Thanks to Townes and Schawlow chapter 10.1 [5] for help refining this argument.)

Returning to the quantum mechanical picture, I believe we can understand this effect somewhat intuitively if we stare long enough at the amplitudes of the spherical harmonics. Note that for a given value of m , Y_{J+1}^m has one more node along the z -axis than Y_J^m . Thus, mixing with $|J+1, m\rangle$ adds a piece of wavefunction that interferes constructively with $|J, m\rangle$ along the positive z -axis but destructively along the negative z -axis, thereby aligning the dipole and lowering its energy. The larger the value of $|m|$ for a given J , the fewer nodes already exist along the z -axis, and so the more effective the interference pattern becomes at aligning the dipole.

5 Induced dipole moment

Problem: Calculate the induced dipole moment d_z for all $J = 0$ and $J = 1$ states in the presence of the perturbing electric field.

Solution: To calculate the energy shift due to an induced dipole, imagine beginning with the molecule in zero electric field where the dipole moment is zero and ramping the field up to its final value of \mathcal{E} . Then the energy shift is given by

$$\Delta E = - \int_0^{\mathcal{E}} \langle d_z(\mathcal{E}') \rangle_{(J,m)} d\mathcal{E}', \quad (21)$$

where the induced dipole $\langle d_z(\mathcal{E}) \rangle_{(J,m)}$ is the expectation value of the dipole operator in the perturbed eigenstates. The energy shift ΔE due to the induced dipole moment is equivalent to the quadratic Stark shift calculated in Section 4. With the benefit of hindsight, we can express this Stark shift as $E_{J,m}^{(2)} = -\alpha(J,m)/2 \times \mathcal{E}^2$, where $\alpha(J,m)$ is a constant of proportionality given by Eq. (20). By substituting this into Eq. (21) differentiating both sides with respect to \mathcal{E} , we obtain

$$\frac{\partial}{\partial \mathcal{E}} \left[-\frac{1}{2} \alpha(J,m) \mathcal{E}^2 \right] = \frac{\partial}{\partial \mathcal{E}} \left[- \int_0^{\mathcal{E}} \langle d_z(\mathcal{E}') \rangle_{(J,m)} d\mathcal{E}' \right] \quad (22)$$

$$\alpha(J,m) \mathcal{E} = \langle d_z(\mathcal{E}) \rangle_{(J,m)}. \quad (23)$$

Thus an induced dipole moment is proportional to the applied electric field with a constant of proportionality α , known as the ‘‘polarizability.’’

We can use Eq. (23) to express the quadratic Stark shift in terms of the dipole moment as $E_{J,m}^{(2)} = -\langle d_z(\mathcal{E}) \rangle_{(J,m)}/2 \times \mathcal{E}$. Solving for the induced dipole moment, we have

$$d_{z(J,m)}(\mathcal{E}) = -\frac{2E_{J,m}^{(2)}}{\mathcal{E}}. \quad (24)$$

Finally, we can use Eq. (20) to calculate the right-hand side of the equation above for all the states in the $J = 0$ and $J = 1$ manifolds and obtain the solutions:

$$d_{z(0,0)}(\mathcal{E}) = \frac{d_{\text{mol}} \mathcal{E}}{\hbar^2/2I} \times \frac{d_{\text{mol}}}{3} \quad (25)$$

$$d_{z(1,0)}(\mathcal{E}) = -\frac{d_{\text{mol}} \mathcal{E}}{\hbar^2/2I} \times \frac{d_{\text{mol}}}{5} \quad (26)$$

$$d_{z(1,\pm 1)}(\mathcal{E}) = \frac{d_{\text{mol}} \mathcal{E}}{\hbar^2/2I} \times \frac{d_{\text{mol}}}{10}. \quad (27)$$

Note that the induced dipole is negative (i.e., anti-aligned with the applied field) for the $|J = 1, m = 0\rangle$ state, where the Stark shift is positive.

6 Rigid rotor in large electric fields

Problem: Explain what would be needed to extend these calculations to larger electric fields, where perturbation theory fails.

Solution: In the non-perturbative limit, we would have to diagonalize the full Hamiltonian to find the Stark-shifted spectrum. From everything we've learned above, we can write down this Hamiltonian as follows:

$$H = \frac{\hbar^2}{2I} J(J+1) |J, m\rangle \langle J, m| + \sqrt{\frac{(J-m+1)(J+m+1)}{(2J+1)(2J+3)}} d_{\text{mol}} \mathcal{E} (|J+1, m\rangle \langle J, m| + |J, m\rangle \langle J+1, m|) + \sqrt{\frac{(J-m)(J+m)}{(2J-1)(2J+1)}} d_{\text{mol}} \mathcal{E} (|J-1, m\rangle \langle J, m| + |J, m\rangle \langle J-1, m|). \quad (28)$$

References

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