Calculation of electric quadrupole linestrengths for diatomic molecules: Application to the $X^1\Sigma^+$ states of H_2 , CO and HF molecules.

W. Somogyi* and S.N. Yurchenko†

*Department of Physics and Astronomy,
University College London, Gower Street,
WC1E 6BT London, United Kingdom*

A. Yachmenev‡

*Center for Free-Electron Laser Science CFEL,
Deutsches Elektronen-Synchrotron DESY, Notkestraße 85,
22607 Hamburg, Germany; Center for Ultrafast Imaging,
Universität Hamburg, Luruper Chaussee 149, 22761 Hamburg, Germany*

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Abstract

We present a unified treatment of the electric quadrupole (E2) matrix elements, Einstein coefficients, and line strengths for general open-shell diatomic molecules in the general purpose DUO spectroscopic program. The implementation has been validated against accurate theoretical calculations and experimental measurements of quadrupole intensities of H_2 available in the literature. Transformation relations between the Cartesian representation (typically used in electronic structure calculations) to the tensorial representation (required for spectroscopic applications) of the electric quadrupole moment components are derived. We also present accurate electronic structure calculations of the electric quadrupole moment functions $\Theta(r)$ for the $X^1\Sigma^+$ states of CO and HF at the CCSD(T) and MRCI levels of theory, respectively. A demonstration of spectroscopic applications is provided by way of infrared E2 line lists for $^{12}\text{C}^{16}\text{O}$ and H^{19}F .

* wilfrid.somogyi.15@ucl.ac.uk

† s.yurchenko@ucl.ac.uk

‡ andrey.yachmenev@cfel.de

I. INTRODUCTION

The electric dipole approximation is often used to treat the spectra of diatomic, or small polyatomic, molecules. For most systems, this is a valid approximation that produces good results. For homonuclear diatomic molecules however, electric dipole (E1) selection rules forbid pure rotational and vibrational transitions, as well as electronic transitions between states of the same symmetry ($u \leftrightarrow u, g \leftrightarrow g$) [1, 2] and electric quadrupole (E2) transitions and magnetic dipole (M1) become important.[3–17]

This has implications for the spectra of several important molecules. The electric dipole transitions are forbidden within the same electronic states, including their ground states. The most famous example is the hydrogen molecule, which despite being the most abundant molecule in the Universe has a very poor electric dipole spectrum. The three lowest lying electronic states of another important molecule, O_2 , all have the same (*ungerade*) symmetry and transitions between them are therefore electric dipole forbidden [7, 18, 19]. Oxygen’s significant absorption in the visible region comes from the electric quadrupole and magnetic dipole moments.

Even when electric dipole transitions are weakly allowed through interactions with other electronic states, E2 and M1 transitions may still be detectable, and their consideration is necessary for an accurate description of the molecule’s spectrum [20–23], such as for the Cameron bands ($a^3\Pi - X^1\Sigma$) and fourth positive system ($A^1\Pi - X^1\Sigma$) of CO [21, 24, 25].

E2 and M1 transitions prove difficult to measure experimentally, owing to their weak intensity and the long path lengths required for appreciable absorption. Electric quadrupole transition moments are on the order of $10^6 - 10^9$ times smaller than electric dipole transition moments [22, 23, 26]. Nevertheless, they are often present in atmospheric spectra, where sufficiently long path lengths are regularly achievable, and play an important role in geophysical and astrophysical applications [5–7, 25, 27, 28].

Many rigorous and robust computational nuclear motion programs exist for computing molecular spectra [29–34], but often the higher order transition moments (E2 and M1) are not considered, or are not rigorously treated. Examples of quadrupole spectra for diatomic molecules include the recent line list of Roueff *et al.* [15]; obtained using high level *ab initio* quadrupole moment and potential energy curves [13, 35] in conjunction with an accurate nuclear motion treatment based on extensive earlier works by Pachucki and Komasa [36–39],

and experimental measurements by Bragg, Brault, and Smith [40] and Campargue *et al.* [41]. In the case of polyatomic molecules, a recent implementation of E2 transitions [22] in the variational nuclear motion program TROVE [42] aided in the first detection of H₂O [22, 23] and CO₂ [43] E2 spectra.

In spectroscopic applications, as used in e.g. the HITRAN database [44], the E2 intensities are usually represented by expressions in terms of effective electric quadrupole moment constants with the rotational line intensities modelled via Hönl-London factors [7, 45]. Here we present a general formulation of the electric quadrupole line intensities for a general (open-shell) diatomic molecule and an implementation of these E2 matrix element and linestrength expressions in the DUO program [46] - a powerful rovibronic variational program developed to compute spectra of diatomics as part of the ExoMol project [47]. The structure of the paper is as follows.

In section II, we outline a unified derivation of the molecular multipole moments starting from the molecular Hamiltonian. We then introduce the rovibronic basis used by the DUO program before presenting expressions for the electric quadrupole matrix elements, linestrengths and Einstein coefficients, for a general case of an arbitrary, open-shell diatomic molecule. We also show how the matrix element components in the Cartesian representation, commonly employed in electronic structure calculations, are related to the tensorial representation used by DUO, and outline the approach taken by DUO to reconstruct the transformation between the two.

In section III we provide demonstrations for the DUO implementation of electric quadrupole linestrength calculations, including a validation against accurate theoretical and experimental linestrengths for H₂. We also present accurate quantum chemistry calculations of the electric quadrupole moment functions for CO and HF molecules, as well as infrared transition linestrengths for ¹²C¹⁶O and H¹⁹F molecules calculated using DUO. These line lists are included into the ExoMol data base www.exomol.com, which aims to provide molecular spectroscopic data for studies of exoplanetary and other atmospheres. More challenging nuclear motion applications of electronic E2 spectra of open-shell diatomic molecules is underway. The spectroscopic model for each molecule, including *ab initio* electric quadrupole moment functions $\Theta(r)$ is made available in the supplementary material via DUO input files. We also provide a list of calculated state energies and quantum numbers, as well cross-sections and line positions in the form of ExoMol `.states` and `.trans` files, and stick spectra.

II. THEORETICAL BACKGROUND

An electromagnetic field described by the scalar and vector potentials ϕ and $\vec{A}$ has electric and magnetic field components $\vec{B} = \nabla \times \vec{A}$ and $\vec{E} = -\nabla\phi - \frac{\partial\vec{A}}{\partial t}$ respectively. The interaction between an external electromagnetic field and a molecular electron, with charge $-e$ and mass m_e , at a point $\vec{r}$, is governed by a Hamiltonian of the form [48]:

$$H = \frac{(\vec{p} + e\vec{A})^2}{2m_e} - e\phi + \frac{e}{2m_e}g_s\vec{B} \cdot \vec{S} + V(\vec{r}, \vec{R}) \quad (1)$$

where $\vec{p}$ is the momentum of the electron, the term $\vec{B} \cdot \vec{S}$ describes the Zeeman interaction between the magnetic field and the electron spin angular momentum, $\vec{S}$ and g_s is the Landé g-factor. The electronic potential energy at position $\vec{r}$ is given by $V(\vec{r}, \vec{R})$, where $\vec{R}$ specifies completely the nuclear geometry of the molecule. If the field is weak, we can neglect the second order field term in Eq. (1). Then, expressing the vector potential as a linear combination of monochromatic plane waves, perturbation theory gives us the probability of a transition between an initial state $|\psi_i\rangle$ and a final state $|\psi_f\rangle$ as

$$P_{f \leftarrow i}(t) = \int_{-\infty}^{\infty} \frac{|A_0(\omega)|^2 t^2}{4\hbar^2} |M_{fi}|^2 \text{sinc}^2 \left[(\omega - \omega_{fi}) \frac{t}{2} \right] d\omega \quad (2)$$

where the transition matrix elements take the form:[49]

$$M_{fi} = \frac{e}{m_e} \langle \psi_f | e^{i\vec{k} \cdot \vec{r}} \hat{\varepsilon} \cdot \vec{p} | \psi_i \rangle \quad (3)$$

where $\hat{\varepsilon} = \vec{A}|\vec{A}|^{-1}$ is the unit vector of the electric field.

A. Multipole Moments

The electric dipole moment approximation is obtained by expanding the exponential term in Eq. (3), and truncating the resulting expression at the first term:

$$e^{i\vec{k} \cdot \vec{r}} = 1 + (i\vec{k} \cdot \vec{r}) + \frac{1}{2}(i\vec{k} \cdot \vec{r})^2 + \dots \approx 1, \quad (4)$$

which is valid when $\vec{k} \cdot \vec{r} \ll 1$ - i.e when the wavelength of the radiation, $\lambda = 1/|\vec{k}|$, is much greater than the length scales of the electronic wavefunction, $|\vec{r}| \sim 10^{-10}$ m. Higher order interactions arise as a result of subsequent terms in the expansion of Eq. (4). In particular,

the second term $(i\vec{k} \cdot \vec{r})$ gives rise to the M1 and E2 moment interactions, for which the matrix element in Eq. (3) becomes:

$$M_{\text{fi}} = \frac{e}{m_e} \langle \psi_{\text{f}} | (i\vec{k} \cdot \vec{r})(\hat{\varepsilon} \cdot \vec{p}) | \psi_{\text{i}} \rangle. \quad (5)$$

The quadruple product identity allows us to separate the matrix element into magnetic and electric components. Using the definition of the magnetic unit vector, $\hat{b} = (\hat{k} \times \hat{\varepsilon})$ and of angular momentum, $\vec{L} = \vec{r} \times \vec{p}$ we can then write the magnetic dipole matrix elements as (assuming a non-zero spin state)

$$\vec{d}_{\text{fi}} = -\frac{e}{2m_e} \langle \psi_{\text{f}} | \hat{L} + g_s \hat{S} | \psi_{\text{i}} \rangle. \quad (6)$$

The orthogonality constraint $\hat{\varepsilon} \cdot \hat{k} = 0$ and Heisenberg's relation allow us to write the electric term in Eq. (5) as

$$(\vec{\varepsilon} \cdot \vec{r})(\hat{k} \cdot \vec{r}) = (\vec{\varepsilon} \cdot \vec{r})(\hat{k} \cdot \vec{r}) - (\varepsilon_x k_x + \varepsilon_y k_y + \varepsilon_z k_z)(r_x r_x + r_y r_y + r_z r_z) \quad (7)$$

$$= \varepsilon_i (r_i r_j - \delta_{ij} \frac{1}{3} r^2) k_j, \quad (8)$$

where Einstein notation implies a summation over all i, j . From which we define the traceless electric quadrupole (E2) moment operator

$$Q_{ij} = -\frac{e}{2m_e} \left(r_i r_j - \delta_{ij} \frac{1}{3} r^2 \right). \quad (9)$$

This derivation of the electric quadrupole moment follows closely that of Buckingham [2], but we present it here as a unified treatment of both the electric quadrupole and magnetic dipole moments.

B. Matrix Elements and Linestrengths

1. Rovibronic wavefunctions

We now consider a calculation of electric quadrupole spectra for an arbitrary (open-shell) diatomic molecule between some generic rovibronic states. Our aim is to implement an E2 spectra module as part of the general diatomic code DUO.[46] DUO uses the Hund's case (a) basis set in the following form:

$$|\varphi_i\rangle = |\xi\Lambda\rangle |S\Sigma\rangle |\xi v\rangle |J\Omega M\rangle \quad (10)$$

where J is the total angular momentum, M is a projection of J on the laboratory Z -axis in units of $\hbar$, S is the total electronic spin angular momentum, Σ is the projection of the spin of electrons on molecular z -axis, ξ are indexes of the ξ -th electronic state, Λ is the projection of the electronic angular momentum on molecular z -axis, $\Omega = \Lambda + \Sigma$ (projection of the total angular momentum on z) and v is the vibrational quantum number.

The original DUO program and its methodology is detailed extensively by Yurchenko *et al.* [46]. For the purpose of defining the matrix elements here, it suffices to simply introduce the definition of the quadrupole moment, the basis functions and the final eigenstates used by the DUO program.

The eigenfunctions corresponding to the final rovibronic eigenvalues are expressed as linear combinations of the basis functions in Eq. (10):

$$|\psi_{JM\tau}\rangle = \sum_{\xi\Lambda\Sigma v\Omega} C_{J\tau}(\xi\Lambda\Sigma v\Omega) |\xi, \Lambda\rangle |S\Sigma\rangle |\xi, v\rangle |J\Omega M\rangle \quad (11)$$

where $C_{J\tau}(\xi\Lambda\Sigma v\Omega) = C_{J\tau}(\varphi)$ are expansion coefficients obtained by solving a system of coupled rovibronic Schrödinger equations variationally, and τ is the symmetry of a rovibronic eigenstate. In case of a heteronuclear diatomic, τ is a parity $\tau = -$ (odd) or $+$ (even), [50] which reflects how $|\psi_{JM\tau}\rangle$ transforms upon inversion or, equivalently, reflection through the molecule-fixed xz plane. For a homonuclear molecule, the symmetry τ includes the parity with respect to the permutation of the nuclei and is traditionally represented by the combinations $+/-$ (xz -reflection) as well as the g/u parities (molecular-fixed inversion), where g and u stand for ‘gerade’ and ‘ungerade’. Generally the good quantum numbers are the total angular momentum J , the symmetry τ and the g and u parities (homonuclear molecules). It is also common to assign other quantum numbers according to the largest coefficient $C_{J\tau}(\varphi)$ in the basis set expansion. [46]

2. Electric Quadrupole Matrix Elements

The Einstein A coefficient for an E2 transition from an initial state i to a final state f is given by: [51, 52]

$$A_{fi} = \frac{8\pi^5(\tilde{\nu}_{fi} \times 10^2)^5}{5\varepsilon_0 h} (2J_i + 1) S(f \leftarrow i), \quad (12)$$

where $\tilde{\nu}_{\text{fi}}$ [cm^{-1}] is the transition wavenumber, ε_0 [Fm^{-1}] is the permittivity of free space, h [Js] is Planck's constant and

$$S(\text{f} \leftarrow \text{i}) = \left| M_{\text{fi}}^{(E2)} \right|^2 = \frac{e^2}{m_e^2} |\langle \psi_{\text{f}} | Q | \psi_{\text{i}} \rangle|^2 \quad (13)$$

is the transition linestrength with unit [$\text{C}^2 \cdot \text{m}^4$] and the matrix elements are those of the quadrupole operator defined by Eq. (9).

The DUO rovibronic wavefunctions $|\psi_{JM\tau}\rangle$, and the transition linestrength in Eq. (13) are defined in the laboratory-fixed frame. Meanwhile, the electric quadrupole moments in Eq. (9) are defined in the molecule-fixed frame. It is therefore convenient to write the electric quadrupole moment in terms of three irreducible tensors $Q^{(0)}$, $Q^{(1)}$ and $Q^{(2)}$ with ranks zero, one and two respectively. The components $Q_m^{(k)}$ with $-k \leq m \leq k$, are expressed in terms of the Cartesian Q_{ij} as:

$$Q_0^{(0)} = -\frac{1}{\sqrt{3}} (Q_{xx} + Q_{yy} + Q_{zz}) \quad (14)$$

$$Q_0^{(1)} = \frac{i}{\sqrt{2}} (Q_{xy} - Q_{yx}) \quad (15)$$

$$Q_{\pm 1}^{(1)} = -\frac{1}{2} [Q_{xz} - Q_{zx} \pm i (Q_{zy} - Q_{yz})] \quad (16)$$

$$Q_0^{(2)} = \frac{1}{\sqrt{6}} (2Q_{zz} - Q_{xx} - Q_{yy}) \quad (17)$$

$$Q_{\pm 1}^{(2)} = \frac{1}{2} [\mp (Q_{xz} + Q_{zx}) - i (Q_{yz} + Q_{zy})] \quad (18)$$

$$Q_{\pm 2}^{(2)} = \frac{1}{2} [(Q_{xx} - Q_{yy}) \pm i (Q_{xy} + Q_{yx})] \quad (19)$$

and transform under rotation between the two frames as follows[50]:

$$Q_m^{(k)} = \sum_{m'} (-1)^{m-m'} Q_{m'}^{(k)} D_{-m-m'}^{(k)} \quad (20)$$

where $D_{-m-m'}^{(k)}$ are the Wigner D -matrices. The traceless definition of the components Q_{ij} (Eq. (9)) and the property of being symmetric under interchange of the indices i, j implies that $Q_0^{(0)} = Q_m^{(1)} = 0$, such that only the second rank components of the quadrupole moment are non-zero. This allows one to write the transition linestrength using the DUO eigenfunctions (Eq. (11)) as

$$S(\text{f} \leftarrow \text{i}) = g_{\text{ns}} \sum_{M_{\text{i}}, M_{\text{f}}} \sum_{m=-2}^2 |\langle \psi_{J_{\text{f}} M_{\text{f}} \tau_{\text{f}}} | Q_m^{(2)} | \psi_{J_{\text{i}} M_{\text{i}} \tau_{\text{i}}} \rangle|^2, \quad (21)$$

where g_{ns} is a nuclear statistical weight that accounts for the degenerate nuclear spin components of the total nuclear-rovibronic wavefunction, see e.g. Bunker and Jensen [53].

Long [54] provides expressions that allows one to construct laboratory frame matrix element expressions for the electric polarisability tensor - also of rank two. Adapting the treatment, one can write the transition quadrupole moment matrix elements as:

$$S(\text{f} \leftarrow \text{i}) = g_{\text{ns}} \left| \sum_{\varphi_{\text{f}}} C_{J_{\text{i}}\tau_{\text{i}}}^*(\varphi_{\text{f}}) \sum_{\varphi_{\text{i}}} C_{J_{\text{f}}\tau_{\text{f}}}(\varphi_{\text{i}}) \sum_{m'} \delta_{S_{\text{f}}S_{\text{i}}} \delta_{\Sigma_{\text{f}}\Sigma_{\text{i}}} \times \right. \\ \left. (-1)^{m'+\Omega_{\text{i}}} \langle v_{\text{f}} | \langle \xi_{\text{f}} \Lambda_{\text{f}} | Q_{m'}^{(2)} | \xi_{\text{i}} \Lambda_{\text{i}} \rangle | v_{\text{i}} \rangle \begin{pmatrix} J_{\text{i}} & J_{\text{f}} & 2 \\ -\Omega_{\text{i}} & \Omega_{\text{f}} & -m' \end{pmatrix} \right|^2, \quad (22)$$

where Eq. (20) was used to transform from the laboratory frame to the molecular frame. Here, m and m' index components of the irreducible representation in the laboratory and molecular reference frames, respectively, and the following properties of the Wigner D -matrices, $D_{-m-m'}^{(k)}$, have been used to express rotational matrix element in terms of the $3j$ -symbols [50]

$$|JM\Omega\rangle = (-1)^{M-\Omega} \left(\frac{2J+1}{8\pi^2} \right)^{\frac{1}{2}} D_{-M-\Omega}^{(J)}, \quad (23)$$

$$\langle JM\Omega| = \left(\frac{2J+1}{8\pi^2} \right)^{\frac{1}{2}} D_{M\Omega}^{(J)}, \quad (24)$$

$$\int D_{cc'}^C D_{aa'}^A D_{bb'}^B \sin \beta \, d\beta \, d\alpha \, d\gamma = 8\pi^2 \begin{pmatrix} A & B & C \\ a & b & c \end{pmatrix} \begin{pmatrix} A & B & C \\ a' & b' & c' \end{pmatrix} \quad (25)$$

with α , β , and γ the Euler angles. Additionally, the following standard property of the $3j$ -symbols implies the $3-j$ symbols containing M_{i} , M_{f} and m , which arise as a result of Eq. (25), can be summed over M_{f} , M_{i} and m and eliminated from Eq. (21)

$$\sum_{m=-k}^k \sum_{M'=-J'}^{J'} \sum_{M''=-J''}^{J''} \left(\begin{pmatrix} J'' & k & J' \\ M'' & m & -M' \end{pmatrix} \right)^2 = 1. \quad (26)$$

If required, e.g for use with molecular dynamics programs such as RICHMOL [55], Duo can explicitly calculate the laboratory frame components of the matrix elements. Note also that the $3j$ -symbols are invariant under cyclic permutations of their columns and have the properties $|A - B| \leq C \leq |A + B|$, and $a + b + c = 0$. Together with the Kronecker deltas in Eq. (22) this implies following selection rules for E2 transitions:

$$\Delta J = J_{\text{f}} - J_{\text{i}} = 0, \pm 1, \pm 2 \quad (27)$$

and $\Delta S = \Delta \Sigma = 0$, such that

$$\Delta \Lambda = \Lambda_f - \Lambda_i = -m = 0, \pm 1, \pm 2 \quad (28)$$

for all $\langle \xi_f \Lambda_f | Q_m^{(2)} | \xi_i \Lambda_i \rangle$ with $-2 \leq m \leq 2$ in Eq. (22). These quantum number selection rules should be supplemented by the symmetry selection rules:

$$+ \leftrightarrow +, \quad - \leftrightarrow - \quad (29)$$

$$g \leftrightarrow g, \quad u \leftrightarrow u. \quad (30)$$

which arise as a result of the symmetric property of the quadrupole moment under coordinate inversion (Eq. (9)), and the requirement that the total matrix element is also symmetric under coordinate inversion, such that the integral over spatial coordinates is non-zero.

3. Representation of *Ab initio* Coupling Curves

The (transitional) quadrupole moments in Eq. (22) are r -dependent curves averaged over electronic coordinates:

$$Q_m^{(2)}(r; \xi_f, \xi_i) = \langle \xi_f \Lambda_f | Q_m^{(2)}(r) | \xi_i \Lambda_i \rangle, \quad (31)$$

where $|\xi_i \Lambda_i\rangle$ and $|\xi_f \Lambda_f\rangle$ are the corresponding electronic wavefunctions. These curves are often computed *ab initio* using electronic structure programs such as MOLPRO[56] or CFOUR[57] used here or empirically by fitting analytical functions to experimental measurements of energies and linestrengths. It is common in electronic structure calculations to represent degenerate symmetry groups for diatomic molecules, namely $C_{\infty v}$ and $D_{\infty h}$ in terms of their Abelian subgroups C_{2v} and D_{2h} .

The irreducible Abelian representation of a matrix element of a given operator coupling initial and final electronic states, each with irreducible Abelian representations G_i and G_f respectively, must be contained within the Abelian group given by the direct product $G_i \times G_f$ [26]. Moreover, it can be shown that there exists only one independent Cartesian quadrupole component coupling a given pair of irreducible representations within an Abelian symmetry group - that which transforms as the product of the two irreducible representations. Tables I and II show the independent quadratic product functions of the Cartesian vectors r_x, r_y, r_z , corresponding to components of the quadrupole moment operator defined

TABLE I. Product table for the quadratic functions and the isotropic function s , that transform as the product of different irreducible representations for the C_{2v} point group.

	A_1	A_2	B_1	B_2
A_1	s	xy	xz	yz
A_2	xy	s	yz	xz
B_1	xz	yz	s	xy
B_2	yz	xz	xy	s

TABLE II. Product table for the quadratic functions and the isotropic function s , that transform as the product of different irreducible representations for the D_{2h} point group.

	A_g	B_{1g}	B_{2g}	B_{3g}	A_u	B_{1u}	B_{2u}	B_{3u}
A_g	s	xy	xz	yz				
B_{1g}	xy	s	yz	xz				
B_{2g}	xz	yz	s	xy				
B_{3g}	yz	xz	xy	s				
A_u					s	xy	xz	yz
B_{1u}					xy	s	yz	xz
B_{2u}					xz	yz	s	xy
B_{3u}					yz	xz	xy	s

by Eq. (9) that transform as the product of each Abelian irreducible representation for the C_{2v} and D_{2h} point groups, respectively.

Equation (22) uses a tensorial representation of all electronic properties, including the electric quadrupole moments $Q_m^{(2)}(r)$. It is also convenient to represent the electronic basis functions $|\xi\Lambda\rangle$ corresponding to doubly degenerate $\Lambda > 0$ states in the tensorial representation with $\pm|\Lambda|$ as a good quantum number. These are related to the Cartesian components $|\alpha\rangle$ and $|\beta\rangle$ by [32]

$$|\xi, \pm|\Lambda|\rangle = \frac{1}{\sqrt{2}} [|\alpha\rangle \pm i|\beta\rangle] \quad (32)$$

where $|\alpha\rangle$ and $|\beta\rangle$ are, for example, $|\Pi_x\rangle$ and $|\Pi_y\rangle$ ($|\Lambda| = 1$), $|\Delta_{xx}\rangle$ and $|\Delta_{xy}\rangle$ ($|\Lambda| = 2$) etc. as typically produced by electronic structure methods.

We now consider the unitary transformation from the Cartesian (‘electronic structure’)

TABLE III. Irreducible representations for homonuclear symmetry groups, their MOLPRO enumeration, and corresponding components of electronic states.

Symmetry	MOLPRO No.	Components
A_g	1	$\Sigma_g^+, (\Delta_g)_{xx}$
B_{1g}	4	$\Sigma_g^-, (\Delta_g)_{xy}$
B_{2g}	6	$(\Pi_g)_x$
B_{3g}	7	$(\Pi_g)_y$
A_u	8	$\Sigma_u^-, (\Delta_u)_{xy}$
B_{1u}	5	$\Sigma_u^+, (\Delta_u)_{xx}$
B_{2u}	3	$(\Pi_u)_y$
B_{3u}	2	$(\Pi_u)_x$

TABLE IV. Irreducible representations for heteronuclear symmetry groups, their MOLPRO enumeration, and corresponding components of electronic states.

Symmetry	MOLPRO No.	Components
A_1	1	Σ^+, Δ_{xx}
A_1	4	Σ^-, Δ_{xy}
B_1	2	Π_x
B_2	3	Π_y

representation of the matrix elements $\langle \xi'' \gamma'' | Q_{ij}(r) | \xi' \gamma' \rangle$ ($\gamma \in [\alpha, \beta]$) to their tensorial ('DUO') representation $\langle \xi'' \Lambda'' | Q_m^{(k)}(r) | \xi' \Lambda' \rangle$ in Eq. (31).

To construct this transformation and also to keep track of the relative phases of 'electronic structure' wavefunctions DUO makes the use of the Cartesian matrix elements of the electronic angular momentum operator $\hat{L}_z$. We choose the Cartesian components $|\alpha\rangle, |\beta\rangle$ such that for wavefunctions with $|\Lambda| > 0$ the $\hat{L}_z$ matrix is given (up to an arbitrary phase factor) by:

$$\mathbf{L}_z = \begin{pmatrix} \langle \alpha | \hat{L}_z | \alpha \rangle & \langle \beta | \hat{L}_z | \alpha \rangle \\ \langle \alpha | \hat{L}_z | \beta \rangle & \langle \beta | \hat{L}_z | \beta \rangle \end{pmatrix} = \begin{pmatrix} 0 & -i\hbar|\Lambda| \\ i\hbar|\Lambda| & 0 \end{pmatrix}, \quad (33)$$

where $\mathbf{L}_z$ is the Cartesian matrix representation of $\hat{L}_z$ with the elements $\langle \xi \gamma'' | L_z | \xi \gamma' \rangle$ and the index ξ is dropped for simplicity. The wavefunctions $|\xi, \pm|\Lambda|\rangle$ in Eq. (32) can be formed

as eigenfunctions of the operator $\hat{L}_z$ in the Cartesian representation by diagonalizing the 2×2 matrix $\mathbf{L}_z$ with the eigenvalues $\hbar|\Lambda|$ and $-\hbar|\Lambda|$. [32] The corresponding unitary matrix that diagonalizes $\mathbf{L}_z$,

$$U = \begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{i}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} & \frac{-i}{\sqrt{2}} \end{pmatrix} \quad (34)$$

provides the transformation between the Cartesian and tensorial representations for any electronic structure property, including the electric quadrupole

$$Q^{\text{tens.}} = U^{-1} Q^{\text{Cart.}} U. \quad (35)$$

Together with the $3j$ -symbol in Eq. (22), which implies that each component $Q_{m'}^{(2)}$ couples electronic states with $\Lambda_f - \Lambda_i = m'$, this allows for the following additional relations to be made

$$\begin{aligned} \langle \pm|\Lambda| | Q_0^{(2)} | \pm|\Lambda| \rangle &= \frac{3}{2\sqrt{6}} \left[\langle \alpha | Q_{zz} | \alpha \rangle + \langle \beta | Q_{zz} | \beta \rangle \right] \\ &= \frac{3}{\sqrt{6}} \langle \alpha | Q_{zz} | \alpha \rangle, \end{aligned} \quad (36)$$

$$\begin{aligned} \langle \Sigma^+ | Q_{\pm 1}^{(2)} | \mp \Pi \rangle &= \mp \frac{1}{\sqrt{2}} \left[\langle \Sigma^+ | Q_{xz} | \Pi_x \rangle + \langle \Sigma^+ | Q_{yz} | \Pi_y \rangle \right] \\ &= \mp \sqrt{2} \langle \Sigma^+ | Q_{xz} | \Pi_x \rangle, \end{aligned} \quad (37)$$

$$\begin{aligned} \langle \Sigma^- | Q_{\pm 1}^{(2)} | \mp \Pi \rangle &= -\frac{i}{\sqrt{2}} \left[\langle \Sigma^- | Q_{xz} | \Pi_y \rangle + \langle \Sigma^- | Q_{yz} | \Pi_x \rangle \right] \\ &= -i\sqrt{2} \langle \Sigma^- | Q_{xz} | \Pi_y \rangle, \end{aligned} \quad (38)$$

$$\begin{aligned} \langle \Sigma^+ | Q_{\pm 2}^{(2)} | \mp \Delta \rangle &= +\frac{1}{\sqrt{2}} \left[\langle \Sigma^+ | Q_{xx} | \Delta_{xx} \rangle + \langle \Sigma^+ | Q_{xy} | \Delta_{xy} \rangle \right] \\ &= +\sqrt{2} \langle \Sigma^+ | Q_{xx} | \Delta_{xx} \rangle, \end{aligned} \quad (39)$$

$$\begin{aligned} \langle \Sigma^- | Q_{\pm 2}^{(2)} | \mp \Delta \rangle &= \pm \frac{i}{\sqrt{2}} \left[\langle \Sigma^- | Q_{xx} | \Delta_{xy} \rangle + \langle \Sigma^- | Q_{yz} | \Delta_{xx} \rangle \right] \\ &= \pm i\sqrt{2} \langle \Sigma^- | Q_{xx} | \Delta_{xy} \rangle, \end{aligned} \quad (40)$$

$$\begin{aligned} \langle \mp \Pi | Q_{\pm 1}^{(2)} | \mp \Delta \rangle &= \mp \frac{1}{2} \left[\langle \Pi_x | Q_{xz} | \Delta_{xx} \rangle + \langle \Pi_x | Q_{yz} | \Delta_{xy} \rangle - \langle \Pi_y | Q_{yz} | \Delta_{xx} \rangle + \langle \Pi_y | Q_{xz} | \Delta_{xy} \rangle \right] \\ &= \mp 2 \langle \Pi_x | Q_{xz} | \Delta_{xx} \rangle, \end{aligned} \quad (41)$$

where both states must have the same g/u symmetry in the case of homonuclear diatomic molecules. The second line in each expression, is obtained by setting matrix elements that

do not satisfy the selection rule Eq. (28) equal to zero and rearranging to obtain relations between different Cartesian components of the matrix elements.

III. DEMONSTRATIONS

In this section we provide a demonstration of the DUO electric quadrupole program for the simple $^1\Sigma$ systems of H_2 , CO and HF. In particular, we choose H_2 as the initial proof of the program due to the highly accurate spectroscopic data available for this molecule, which we aim to reproduce. The demonstrations for CO and HF exemplify heteronuclear systems with large molecular quadrupole moments in which the consideration of E2 transitions is necessary to obtain accurate cross-sections. All three systems considered here are closed-shell ground electronic states, such that $\Lambda = S = 0$. The spectroscopic models detailed in this section are provided as supplementaries in the form of DUO input files, the DUO program itself is open-source and can be obtained from the ExoMol public repository at github.com/Exomol.

A. Molecular Hydrogen

Molecular hydrogen is the simplest diatomic molecule, containing just two electrons and two protons. It is the most abundant molecule in the universe and plays an important role in star formation, [59–62] interstellar physics, [63–65] (exo)planetary atmospheres, [66–69] and investigations of fundamental physics.[70, 71]

Owing to its molecular symmetry, the homonuclear H_2 molecule has no permanent electric dipole moment, and thus rovibrational transitions are forbidden in the electric dipole approximation. The availability of highly accurate electronic potential energy curves (PECs) and electric quadrupole moment curves (QMCs) makes H_2 an ideal candidate for validating the implementation of E2 transitions in DUO. The simplicity of the H_2 molecule makes it an extremely tractable quantum mechanical problem - indeed, it was the model molecule for many early calculations of molecular dynamics, on the world’s first mass-produced computers.[72–74] Even for these early calculations linestrength accuracies within a few percent were attainable.[75–77] As a result, there is a wealth of accurate spectroscopic data available with which the DUO implementation can be validated. Most recently, Roueff *et al.* [15] cal-

culated a highly accurate (order 10^{-6} cm^{-1}) infrared spectrum for the H_2 molecule, including adiabatic, nonadiabatic, relativistic, and quantum electrodynamic corrections.[39, 78]

The calculations of Roueff *et al.* [15] are based on an extensive series of earlier works by Pachucki [35], Pachucki and Komasa [36, 37, 38], in which the H_2 Born-Oppenheimer PEC was obtained with 10^{-15} relative numerical precision using 22,000 exponential basis functions and explicit electron correlation calculations [35, 79]. They also compute non-adiabatic[36, 38], adiabatic[37] and high-order relativistic [80] corrections to the Born-Oppenheimer potential energy. The quadrupole moment function employed in their calculations is obtained using the Born-Oppenheimer wavefunction, and is in agreement with the values reported by Wolniewicz, Simbotin, and Dalgarno [13], who employ a 494-terms correlated basis representation of the wavefunction to obtain the quadrupole moment function with an estimated accuracy on the order of 0.001%.

For the validation of the DUO implementation, we retrieve their original Born-Oppenheimer potential using the **V(DR)** function made available via the H2SPECTRE program.[78] The contribution of the adiabatic and non-adiabatic corrections computed by Roueff *et al.* [15] are in the range $5\text{--}20 \text{ cm}^{-1}$ and $0.4\text{--}4.0 \text{ cm}^{-1}$, respectively, increasing the total state energy. The higher order relativistic corrections are on the order of 0.01 cm^{-1} or less. Since the Born-Oppenheimer PEC provided does not include adiabatic or non-adiabatic corrections, we expect to see significant deviation in the calculated state energies for high v and J states. Typically these deviations could be corrected in DUO via an empirical fit to experimentally accurate state energies. We do not perform such a refinement in this work, as our aim is not to provide an accurate or improved line list for H_2 , but to illustrate the implementation of E2 transition strengths. We also employ the quadrupole moment function of Wolniewicz, Simbotin, and Dalgarno [13], given as a grid of 253 E2 moment values between $0.2\text{--}20.0 a_0$, which DUO interpolates using quintic splines.

The vibrational grid is defined by 501 equally spaced points in the range $0.2\text{--}10.0 \text{ \AA}$. After solving the vibrational Schrödinger using the sinc-DVR method, we selected the first 30 vibrational states to form the contracted vibrational basis. The threshold for intensity cut-off is $10^{-99} \text{ cm}^2 \text{ molecule}^{-1}$, and we solve the rovibrational Schrödinger equation for rotational states with total angular momentum quantum numbers $0 \leq J \leq 200$ at 296 K.

In Figure 1 we illustrate the results of a line-by-line comparison of the DUO results to the accurate line list of Roueff *et al.* [15] (including all corrections). As expected we see

FIG. 1. Agreement between the Einstein-A coefficients (bottom-left) and state energies of H_2 calculated by DUO (A_{if}, E), and by Roueff *et al.* [15] ($\bar{A}_{\text{if}}, \bar{E}$). The colors in each plot correspond to the (final) vibrational quantum number of the state.

significant differences between the energies calculated by DUO (E) and the accurate energies provided by H2SPECTRE ($\bar{E}$) for high v , J states. These differences are most significant for states with $v \geq 10$, and hence we exclude these vibrational states from the following analysis. For transitions between the remaining vibrational levels, we find that 93.3% of our Einstein coefficients (A_{fi}) lie within 1% of the values calculated by Roueff *et al.* [15] ($\bar{A}_{\text{fi}}$). The 99-th percentile is $|1 - A_{\text{fi}}/\bar{A}_{\text{fi}}| = 0.0670$. For transitions less than $20\,000\text{ cm}^{-1}$ in energy, the 99-th percentile is $|1 - A_{\text{fi}}/\bar{A}_{\text{fi}}| = 0.0023$, the mean is $|1 - A_{\text{fi}}/\bar{A}_{\text{fi}}| = 0.0021$ and 98.6% of Einstein coefficients lie within 1% of the values calculated by Roueff *et al.* [15].

Figure 2 shows a direct comparison between the Einstein coefficients predicted by Roueff *et al.* [15] and those obtained via the DUO quadrupole implementation. We also illustrate the absorption intensities obtained from the DUO results via the EXOCROSS program, as compared to transitions listed in the HITRAN[44] database. In Table V we compare the results of the calculation to the experimentally measured intensities and line position of Bragg, Brault, and Smith [40], and in Table VI to more recent measurements of Campargue *et al.* [41], as well as their theoretical predictions based on the effective quadrupole moment method. The Duo calculated intensities reproduce closely the accurate experimental measurements of Campargue *et al.* [41], and match their theoretical predicted values to within 0.1. Agreement with the older measurements of Bragg, Brault, and Smith [40] are less consistent but generally agree, particularly for the Q -branch transitions of the first overtone band. In both cases the line positions differ considerably, but by a roughly constant value across each vibrational band. This is due to the fact that we do not perform the DUO refinement procedure or account for any adiabatic or non-adiabatic corrections in our calculations.

FIG. 2. Comparison of the DUO calculated Einstein coefficients with the target values predicted by Roueff *et al.* [15] (left), and of the DUO calculated absorption intensities with the intensities listed in the HITRAN database[13, 44, 81] (right).

TABLE V. Comparison of various H_2 $v' \leftarrow 0$ transitions (positions and intensities), measured experimentally by Bragg, Brault, and Smith [40], to the values predicted by DUO calculations at $T = 296$ K.

v'	Branch	$\tilde{\nu}_{\text{obs.}} - \tilde{\nu}_{\text{calc.}}$ (cm^{-1})	$I_{\text{obs.}}/I_{\text{calc.}}$
1	Q(3)	-1.158	1.080
1	Q(2)	-1.165	1.027
1	Q(1)	-1.171	1.040
1	S(0)	-1.181	1.158
1	S(1)	-1.185	1.648
1	S(2)	-1.185	1.594
1	S(3)	-1.187	1.013
2	O(3)	-2.121	0.852
2	O(2)	-2.138	0.915
2	Q(3)	-2.121	0.949
2	Q(2)	-2.136	0.973
2	Q(1)	-2.147	1.624
2	S(0)	-2.152	0.984
2	S(1)	-2.147	0.988
3	S(0)	-2.923	0.816
3	S(1)	-2.912	0.911
3	S(2)	-2.887	1.017
3	S(3)	-2.858	0.878
4	S(0)	-3.480	0.606
4	S(1)	-3.469	0.874
4	S(2)	-3.432	0.727
4	S(3)	-3.382	0.831

TABLE VI. Comparison of various H_2 $v' = 2 \leftarrow 0$ overtone lines, measured experimentally and computed via an effective quadrupole moment by Campargue *et al.* [41], and the values predicted by DUO calculations for $T = 296$ K.

Branch	$\tilde{\nu}_{\text{obs.}} - \tilde{\nu}_{\text{calc.}}$	$I_{\text{obs.}}/I_{\text{calc.}}$	$\tilde{\nu}_{\text{obs.}} - \tilde{\nu}_{\text{calc.}}^{\text{DUO}}$	$I_{\text{obs.}}/I_{\text{calc.}}^{\text{DUO}}$
O(5)	-0.0019	0.924	-2.061	0.924
O(4)	-0.0040	0.931	-2.093	0.930
O(3)	-0.0033	1.008	-2.115	1.007
O(2)	-0.0031	1.001	-2.132	1.000
O(5)	-0.0030	1.020	-2.067	1.020

B. Carbon Monoxide

Carbon monoxide is a heteronuclear diatomic molecule, and thus electric dipole transitions are allowed within its ground $X^1\Sigma^+$ state. However, it also possesses a strong electric quadrupole moment, $\Theta = -1.95(7)$ a.u. [$a_0 e^2$] and, as a result, the electric dipole infrared

spectrum is accompanied by weaker electric quadrupole lines. As we will show, many of the E2 spectral lines at room temperature lie higher in intensity than the minimum spectroscopic cutoff of 10^{-30} cm/molecule, typically applied to E1 spectra. As a result, their inclusion or emission in spectroscopic databases has significant implications for applications where accurate cross-sections are required.

Numerous experimental and *ab initio* studies have been performed of the electric dipole moment spectra for the CO molecule, including recent accurate calculations by Li *et al.* [82]. Li *et al.* seek to resolve a long-standing uncertainty in the line intensities of CO E1 spectra, namely significant differences observed between the intensities predicted by the calculations of Goorvitch [83] and those of Huré, J. M. and Roueff, E. [84]. The former uses Chackerian’s [85] semi-empirical dipole moment function, obtained from a nonlinear least-squared fit to vibrational states up to $v = 38$. The latter uses a purely *ab initio* electric dipole moment curve (DMC), computed by Langhoff and Bauschlicher via ACPF calculations on a 5Z basis set [86]. Li *et al.* perform new CRDS measurements in order to produce an accurate DMC via a direct-fit. At long equilibrium bond lengths, where experimental data is not attainable, they reproduce the calculations of Langhoff and Bauschlicher [86] but with a finer grid, and determine that the interpolation used on the original grid was insufficient to capture the full shape of the DMC. Their PEC of choice is the analytical MLR3 function obtained by Coxon and Hajigeorgiou [87] via a direct fit to 21559 spectroscopic lines [87].

Studies of the quadrupole moment of CO are somewhat sparser. Although several experimental measurements exist for the equilibrium molecular quadrupole moment, only a single study presents an QMC across a range of geometries. The early work by Truhlar [88] presents simple Hartree-Fock calculations of the quadrupole moment at just 6 internuclear geometries. The accuracy of the vibrational matrix elements calculated is low, particularly for weaker transitions corresponding to higher vibrational quantum numbers. In particular the methodology struggles to accurately describe the quadrupole moment at long internuclear distances, which are necessary for calculating the vibrational overtones. Coriani *et al.* [89] compares the results of CCSD and CC3 calculations on the CO molecule with a variety of basis sets. The results show that the CCSD level of theory is insufficient to correctly describe the electric properties of the CO molecule, and that consideration of triple excitations is vital. They also study the convergence of such calculations with increasing basis set size, and find the results converge quickly for bases larger than DZ.

FIG. 3. Electric quadrupole moments for CO obtained in this work via CCSD(T) calculations compared to Hartree-Fock calculations by Truhlar [88].

Following the success of Coriani *et al.* [89], we employ the CCSD(T) method with an aug-cc-pwCVQZ basis as implemented in the CFOUR program [57] to calculate the strength of the non-zero quadrupole component Q_{zz} for 100 nuclear geometries in the range 0.86–2.16 Å. The QMC obtained from these calculations is shown in Figure 3. Divergent behaviour at large internuclear separations is attributed to CCSD(T)’s inability to account for multireference effects. The curve is therefore truncated between 0.8–1.6 Å.

The value of the electric quadrupole moment at equilibrium separation $\Theta = -1.45$ a.u. agrees well with other values from the literature, as shown in Table VII. Note that Truhlar [88] chooses a definition of the quadrupole moment which is a factor of two larger than the definition employed by MOLPRO and DUO we quote half that value here.[88]

Also obtained from the CCSD(T) calculations is the PEC for the ground $X^1\Sigma^+$ state, however we instead perform the nuclear motion calculations with the semi-empirical PEC of Meshkov *et al.* [92], which has the following form:[92]

$$U(\beta, r) = Y(r)\Lambda(\beta, z(r)) \quad (42)$$

where $Y(r)$ accounts for the asymptotic behaviour of the potential in both the short- and

TABLE VII. A comparison of equilibrium values of the *ab initio* electric quadrupole moment of CO.

Θ / a.u.	Method	Ref.
-1.4522	CCSD(T)	This work
-1.443(69)	EFGIB	90
-1.385(31)	EFGIB	90 and 91
-1.18(25)	EFGIB	1 and 90
-1.445(2)	CC3	89
-1.3315	HF	88

long-range limits;

$$Y(r) = Y_0(r) + Y_\infty(r), \quad (43)$$

$$Y_0(r) = \left[\frac{K}{r} + Kd_0 + E_0 + \left(\frac{1}{2}Kd_0 + E_0 \right) d_0 r \right] \exp(-d_0 r), \quad (44)$$

$$Y_\infty(r) = \sum_{n=5,6,8} D_n(r) \frac{C_n}{r^n}, \quad (45)$$

where $D_n(r)$ is a modified Douketis damping function[93]

$$D_n(r) = \left[1 - \exp \left(-\frac{d_1}{n} r - \frac{d_2}{\sqrt{n}} r^2 \right) \right]^{n+2} \quad (46)$$

and the mapping function $z(r)$ is chosen as

$$z(r) = \tanh(c_1 r - c_2 r^{-1}) \quad (47)$$

with $d_{0,1}$ and $c_{1,2}$ constants. The function $\Lambda(\beta, z)$ is non-singular in the domain $z \in [-1, +1]$, and is represented as a Chebyshev polynomial of the first kind,

$$\Lambda(\beta, z) = \sum_{n=0}^N \beta_n T_n(z). \quad (48)$$

The details of this analytical function and the fitting procedure are given by Meshkov *et al.* [92]. We choose this accurate analytical representation of PEC for our DUO solutions in order to improve the quality of the wavefunctions used to calculate the linestrengths.

The DUO vibrational grid used for the calculation consists of 501 equally spaced points in the range 0.7–3.0 Å, and we select the first 45 vibrational states to form the contracted basis. After solving the Schrödinger equation for rotational quantum numbers $0 \leq J \leq 200$, we discard transitions with a transition quadrupole $\Theta < 1 \times 10^{-5}$ a.u.. It was found by Medvedev *et al.* [94] that for large changes in vibrational quanta, numerically computed transition moments are sensitive to the asymptotic behaviour of the PECs and coupling curves. In particular, representing the coupling as a grid of *ab initio* points, and applying spline interpolation to obtain the value of the coupling on the vibrational grid, results in discontinuities in the derivative of the coupling. For electric dipole transitions, performing a simultaneous fit to both the empirical and *ab initio* values can be an effective solution, using long-range *ab initio* data to constrain the asymptotic behaviour of the curves. In the case of electric quadrupole transitions however, the intensity of these high overtone vibrational bands is sufficiently weak ($< 10^{-32}$ cm² molecule⁻¹) that absorption lines with transition quadrupole moments $\Theta < 1 \times 10^{-5}$ a.u. (corresponding to high overtone bands) can simply be excluded from the line list altogether.

FIG. 4. The first 6 vibrational bands (left) and infrared rotational bands (right) of the E1 and E2 rovibrational spectrum in the ground $X^1\Sigma^+$ state of the $^{12}\text{C}^{16}\text{O}$ molecule. The E1 intensities are those of Li *et al.* [82], via the ExoMol database.

After solving the Schrödinger equation we substitute the calculated state energies for those obtained by Li *et al.* [82] in a simultaneous direct-fit to experimentally determined energy levels. This improves the accuracy in the line positions of the final stick spectrum,

f	i	A_{fi}	$\tilde{\nu}_{fi}$
94	10	1.0587E-17	10.591935
93	9	1.1546E-17	10.696876
92	8	1.2569E-17	10.801832
91	7	1.3657E-17	10.906802
90	6	1.4815E-17	11.011786
89	5	1.6043E-17	11.116781
88	4	1.7346E-17	11.221787
87	3	1.8725E-17	11.326802
86	2	2.0183E-17	11.431825
85	1	2.1722E-17	11.536856
136	52	1.7502E-16	17.652735

TABLE VIII. Extract from the $^{12}\text{C}^{16}\text{O}$ electric quadrupole Transition file. It contains the upper (f) and lower (i) states counting numbers, Einstein A coefficients (s^{-1}) and transition wavenumbers (cm^{-1}).

obtained via EXOCROSS[95], but has no effect on the quadrupole Einstein coefficients or linestrengths. The energy level data of Li *et al.* [82] is made available through the HITRAN or ExoMol (exomol.com) databases [47]. The resultant room temperature ($T = 296$ K) spectrum is illustrated in Figure 4, where it is compared to the E1 spectrum of Li *et al.* [82]. The difference is approximately eight orders of magnitude. Nonetheless, many E2 lines - particularly for the $v = 0 \leftarrow 0$ and $v = 1 \leftarrow 0$ bands - lie above the typical cutoff intensity used in many spectroscopic databases ($\sim 10^{-30} \text{ cm}^2 \text{ molecule}^{-1}$).

The computed electric quadrupole Einstein A coefficients of $^{12}\text{C}^{16}\text{O}$ are combined with the ExoMol line list Li2015 for CO in a form of the Transition file, see an extract in Table VIII. Apart from the Einstein A coefficients (s^{-1}), a Transition file provides the upper and lower state counting numbers as listed in an ExoMol State file, as illustrated in Table IX, which presents an extract from the ExoMol State file of the $^{12}\text{C}^{16}\text{O}$ line list Li2017. For more details on the ExoMol line list structure see Tennyson *et al.* [47].

TABLE IX. Extract from the Li2017 States file for $^{12}\text{C}^{16}\text{O}$.

i	E	g	J	v	e/f
1	0.000000	1	0	0	e
2	2143.271100	1	0	1	e
3	4260.062200	1	0	2	e
4	6350.439100	1	0	3	e
5	8414.469300	1	0	4	e
6	10452.222200	1	0	5	e
7	12463.768600	1	0	6	e
8	14449.181300	1	0	7	e
9	16408.534600	1	0	8	e
10	18341.904400	1	0	9	e
11	20249.368200	1	0	10	e

i : State counting number.

$\tilde{E}$: State energy in cm^{-1} .

g_i : Total statistical weight, equal to $g_{\text{ns}}(2J + 1)$.

J : Total angular momentum.

State: Electronic state.

v : State vibrational quantum number.

e/f : Rotationless parity.

C. Hydrogen Fluoride

Like the CO molecule, HF possesses a strong permanent electric dipole moment, $\mu = 1.8195(26)$ D [96], it also possesses a strong permanent electric quadrupole moment, $\Theta = 1.750(2)$ a.u. [97]. Numerous *ab initio* studies have been performed for HF, including several which produce QMCs for the ground $X^1\Sigma^+$ electronic state [98–100]. Piecuch *et al.* [98] use the orthogonally spin-adapted linear-response coupled-cluster (LRCC) theory with singly and doubly excited clusters (CCSD) and obtain quadrupole moments at 15 internuclear geometries in the range 1.126 32–12.1296 a.u. Their basis set of choice is that introduced by Sadlej for correlated calculations of molecular electric properties[101], which they compare

to standard basis sets at the TZ level. They also provide the results of full CI calculations on a DZ basis set. Maroulis [99] presents all-electron CCSD(T) calculations of the quadrupole moment at nine internuclear geometries in the range 0.9328–2.5328 a.u. For comparison, we compute the quadrupole moment for the $X^1\Sigma^+$ state via MRCI method and an aug-cc-pVQZ basis set at 501 internuclear geometries in the range 0.7–3.7 Å using MOLPRO.

TABLE X. A comparison of molecular quadrupole moments for HF.

Θ / a.u. Method	Ref.
1.705 6 MRCI	This work
1.715 7 CCSD	98
1.71 CCSD(T)	99
1.75(2) MBERS	97 and 102

The quadrupole moments obtained via these various methods are illustrated in Figure 7. All four calculations produce similar values for $\Theta(R_e)$, but systematically underestimate the strength relative to experimental measurements. The CCSD calculations of Piecuch *et al.* [98] show the closest agreement with the experimental uncertainty of de Leeuw and Dymanus’ measurements [97]. Although the four curves have the same general shape, significant variation is apparent between the value of Θ computed at intermediate bond lengths close to 2 Å. Here the strength of the quadrupole moment is greatest, and difference of more than 0.5 a.u. is apparent between the full CI and CCSD methods.

For the PEC, Coxon and Hajigeorgiou [103] provide a very accurate RKR-style analytical expression for the potential energy and Born-Oppenheimer breakdown functions of the $X^1\Sigma^+$ ground electronic state of various hydrogen halide isotopologues, including H⁹F. They devise a novel analytical form (MLR3) of the diatomic electronic potential and perform a non-linear least squares fit to experimental energies. The MLR3 function is given by [104]:

$$V(r) = D_e \left(1 - \frac{u_{\text{LR}}(r)}{u_{\text{LR}}(r_e)} \exp[-\phi_{\text{MLR3}}(r)y_{p,a}(r, r_e)] \right)^2, \quad (49)$$

where

$$y_{p,a}(r, r_e) = \frac{r^p - r_e^p}{r^p - ar_e^p} \quad (50)$$

FIG. 5. Comparison of the quadrupole moment curves for HF obtained via various *ab initio* methods. The MRCI calculations presented in this work, CCSD(T) calculations of Maroulis [99], and CCSD and full-CI calculations of Piecuch *et al.* [98].

and the long-range potential function $u_{\text{LR}}(r)$ is given by:

$$u_{\text{LR}}(r) = \sum_n D_n(r) \frac{C_n}{r^n}, \quad (51)$$

Coxon and Hajigeorgiou [104] propose generalised Douketis damping [93] or Tang-Toennies Tang and Toennies [105] damping functions for $D_n(r)$, the DUO implementation of MLR3 employs Douketis damping functions defined as:

$$D_n(r) = \left(1 - \exp \left[-\frac{b(s)(\rho r)}{n} - \frac{c(s)(\rho r)^2}{\sqrt{n}} \right] \right)^{m+s}, \quad (52)$$

with $\rho = 2\rho_A\rho_B/(\rho_A + \rho_B)$ for atoms A, B where $\rho_{A,B} = (I_p^{A,B}/I_p^{A,B})^{2/3}$ and I_p^H is the ionisation potential of the hydrogen atom. Lastly the function $\phi_{\text{MLR3}}(r)$ is given by:

$$\phi_{\text{MLR3}}(r) = y_m(r, r_{\text{ref}})\phi_{\text{MLR3}}(\infty) + [1 - y_m(r, r_{\text{ref}})] \sum_{i=0}^{N_\phi} \phi_i y_q(r, r_{\text{ref}})^i, \quad (53)$$

where

$$y_{m,q}(r, r_{\text{ref}}) = \left(\frac{r^{m,q} - r_{\text{ref}}^{m,q}}{r^m + r_{\text{ref}}^{m,q}} \right), \quad (54)$$

$$\phi_{\text{MLR3}}(\infty) = \ln \left(\frac{2D_e}{u_{\text{LR}}(r_e)} \right). \quad (55)$$

FIG. 6. Comparison of the potential energy curves for the $X^1\Sigma^+$ ground state of HF. The MRCI^a calculations are from this work, empirically fitted MLR3^b potential of Coxon and Hajigeorgiou [103], and the CCSD^c calculations of Piecuch *et al.* [98].

This analytical representation of the MLR3 potential has been newly implemented in DUO and for the present calculations, we employ the HF MLR3 parameters obtained by Coxon and Hajigeorgiou [103], as well as their Born-Oppenheimer breakdown (BOB) function which is obtained from the Fortran source code provided in the supplementary material of Coxon and Hajigeorgiou [103].

In Figure 6, we show a comparison of the potential energy curves obtained from our MRCI calculations, the CCSD calculations of Piecuch *et al.* [98] and the MLR3 potential of Coxon and Hajigeorgiou [103]. All three methods give similar results at short and intermediate bond lengths. The CCSD calculations overestimate the dissociation energy, relative to the empirical MLR3 potential, and the MRCI results predict a slightly lower dissociation energy. In Figure 7 we illustrate the results of calculations from two spectroscopic models. In each case the potential energies are the same; the MLR3 and BOB curves of Coxon and Hajigeorgiou [103]; but in one model we use our own MRCI quadrupole moment, and in the other we use Piecuch’s CCSD quadrupole moment. In both cases we perform calculations for rotational states $0 \leq J \leq 400$, the vibrational grid is defined for 501 equally spaced points in the range 0.4–4.4 Å, and we choose the first 45 vibrational states for the contracted basis.

For the first three vibrational bands, the absorption intensities predicted by both spectroscopic models are nearly identical. Higher order vibrational bands, however, exhibit

FIG. 7. Comparison of the electric quadrupole absorption spectrum for H^{19}F obtained via spectroscopic models using the CCSD and MRCI quadrupole moment curves illustrated in Figure 5.

significant discrepancies. The CCSD intensities begin to plateau above $20\,000\text{ cm}^{-1}$, we propose that this intensity plateau arises as a result of the same effect encountered in section III B and detailed by Medvedev *et al.* [94]. Comparatively, the MRCI spectrum shows no such intensity plateau, indeed the MRCI quadrupole moment is obtained on a considerably finer grid spacing, which aids in smoothing the interpolation. A second possible cause proposed by Medvedev *et al.* [94] is the asymptotic behaviour of the quadrupole moment curves at longer internuclear distances. Here the magnitude of the coupling becomes exponentially smaller, and significant relative variations in the gradient of Θ are observed between the two methods. The gradient of CCSD quadrupole moment curve at distances $R > 3$ decays considerably slower than that obtained via MRCI calculations. In Figure 8 we show the gradient of the two quadrupole moment functions computed using a central finite difference scheme on the Duo integration grid. It illustrates that the CCSD quadrupole moment has a gradient approximately two orders of magnitude larger than that of the MRCI calculations at long internuclear distances.

The MRCI spectrum exhibits a local minimum in intensity for the $v = 5 \leftarrow 0$ band. A similar abnormal intensity was observed by Medvedev *et al.* [94] for the same vibrational band of the electric dipole spectrum. Regardless, the expected E2 absorption intensities for the $v = 5 \leftarrow 0$ band is extremely weak, and below typical spectroscopic cutoff intensity

FIG. 8. Central finite difference gradients of the MRCI and CCSD quadrupole moment functions with respect to internuclear distance.

(10^{-30} cm/molecule).

FIG. 9. The first 10 vibrational bands (left) and rotational $v = 0 - 1$ transitions (right) of the E1 and E2 rovibrational spectrum in the ground $X^1\Sigma^+$ state of the H^{19}F molecule. The E1 spectrum is that of Coxon and Hajigeorgiou [103], via the ExoMol database.

IV. CONCLUSIONS

Generic expressions for the electric quadrupole Einstein coefficients and matrix elements between arbitrary electronic states of (open-shell) diatomic molecules have been derived and implemented in the DUO spectroscopic code. The implementation is general, and allows for the creation of highly accurate *ab initio* and empirical spectroscopic models and line lists for an array of astrophysically important molecules. The work has been validated by reproducing highly accurate literature data for the homonuclear H₂ molecule, and further demonstrated by the calculation of novel electric quadrupole spectra for the heteronuclear CO and HF molecules. The line lists for ¹²C¹⁶O and H¹⁹F have been included into the ExoMol data base.

Through this calculation, we have shown that even for electric dipole-allowed systems, electric-quadrupole line intensities can often lie above the typically cutoff intensities used in spectroscopic databases, atmospheric retrievals and remote-sensing applications. For many homonuclear systems where rovibrational, and many electronic, transitions are forbidden in the electric dipole approximation, calculation of the quadrupole intensities is crucial for producing accurate rovibronic line lists. Our goal is to provide accurate E2 and M1 line lists for electronic transitions of open-shell diatomic molecules such as O₂, N₂, SO etc.

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V. DATA AVAILABILITY STATEMENT

The data that supports the findings of this study are available within the supplementary material and are also openly available at www.exomol.com.

Appendix A: Supplementary material

1. `1H2_E2.inp` - DUO input file for H₂ spectroscopic model, detailed in section III A.
2. `1H2_E2.states` - ExoMol format `.states` file, containing DUO quantum numbers and calculated energies for the $X\ ^1\Sigma^+$ state of H₂.
3. `1H2_E2.trans` - ExoMol format `.trans` file, containing DUO calculated line positions and intensities for rotation-vibration transitions in the $X\ ^1\Sigma^+$ state of H₂.
4. `1H2_E2.stick` - ExoMol format stick spectrum for electric quadrupole transitions in the $X\ ^1\Sigma^+$ state of H₂.
5. `12C-16O_Li2015_E2.inp` - DUO input file for spectroscopic model, detailed in section III A.
6. `12C-16O_Li2015.states` - ExoMol format `.states` file from the electric dipole linelist of Li *et al.* [82], containing DUO quantum numbers and calculated energies for the $X\ ^1\Sigma^+$ state of CO.
7. `12C-16O_Li2015_E2.trans` - ExoMol format `.trans` file, containing DUO calculated line positions and intensities for rotation-vibration transitions in the $X\ ^1\Sigma^+$ state of.
8. `12C-16O_Li2015_E2.stick` - ExoMol format stick spectrum for electric quadrupole transitions in the $X\ ^1\Sigma^+$ state of H₂.
9. `1H-19F_Coxon-Hajig_E2.inp` - DUO input file for H¹⁹F spectroscopic model, detailed in section III A.
10. `1H-19F_Coxon-Hajig.states` - ExoMol format `.states` file from the electric dipole linelist of Coxon and Hajigeorgiou [103], containing DUO quantum numbers and calculated energies for the $X\ ^1\Sigma^+$ state of H¹⁹F.
11. `1H-19F_Coxon-Hajig_E2.trans` - ExoMol format `.trans` file, containing DUO calculated line positions and intensities for rotation-vibration transitions in the $X\ ^1\Sigma^+$ state of H¹⁹F.
12. `1H-19F_Coxon-Hajig_E2.stick` - ExoMol format stick spectrum for electric quadrupole transitions in the $X\ ^1\Sigma^+$ state of H¹⁹F.

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