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Topical Review

The *ab initio* calculation of spectra of open shell diatomic molecules

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Abstract
The spectra (rotational, rotation–vibrational or electronic) of diatomic molecules due to transitions involving only closed-shell ($^1\Sigma$) electronic states follow very regular, simple patterns and their theoretical analysis is usually straightforward. On the other hand, open-shell electronic states lead to more complicated spectral patterns and, moreover, often appear as a manifold of closely lying electronic states, leading to perturbed spectra of even greater complexity. This is especially true when at least one of the atoms is a transition metal. Traditionally these complex cases have been analysed using approaches based on perturbation theory, with semi-empirical parameters determined by fitting to spectral data. Recently the needs of two rather diverse scientific areas have driven the demand for improved theoretical models of open-shell diatomic systems based on an *ab initio* approach; these areas are ultracold chemistry and the astrophysics of 'cool' stars, brown dwarfs and most recently extrasolar planets. However, the complex electronic structure of these molecules combined with the accuracy requirements of high-resolution spectroscopy render such an approach particularly challenging. This review describes recent progress in developing methods for directly solving the effective Schrödinger equation for open-shell diatomic molecules, with a focus on molecules containing a transtion metal. It considers four aspects of the problem: (i) the electronic structure problem; (ii) non-perturbative treatments of the curve couplings; (iii) the solution of the nuclear motion Schrödinger equation; (iv) the generation of accurate electric dipole transition intensities. Examples of applications are used to illustrate these issues.

Keywords: spectroscopy, ultracold molecules, transition metal compounds, lifetimes, spin–orbit coupling, vibronic spectra

(Some figures may appear in colour only in the online journal)

1. Introduction

New and powerful experimental techniques to produce and study ultra-cold molecules (below 1 mK) are becoming increasingly available as recently reviewed by Hamamda *et al* (2015). These techniques include combining two ultra-cold atoms (Bergeman *et al* 2003, Juarros *et al* 2006, Ulmanis *et al* 2012, Pazyuk *et al* 2015), direct laser cooling (Shuman *et al* 2010, Glöckner *et al* 2015), deceleration techniques (Hogan *et al* 2011), cooling (Stuhl *et al* 2012), magneto-optical trapping (Hummon *et al* 2013, Barry *et al* 2014) and buffer-gas cooling (Hutzler *et al* 2012). This has stimulated new interest in the detailed spectroscopy of open shell diatomic systems (Di Rosa 2004, Quéméner 2012). Similarly, but at significantly higher temperatures, the study of molecules in the atmospheres of brown dwarfs and cool stars requires comprehensive datasets of spectral absorptions by a range of diatomic species whose vibronic transitions absorb

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near the peak flux of the object under study (Rajpurohit *et al* 2013). Similar species are also thought to be important constituents of the atmospheres of hot exoplanets (Ali-Dib *et al* 2014, Stevenson *et al* 2014), although there are as yet no confirmed observations of such spectra from a specific molecule. The spectra of these species also provide important diagnostics for those interested in probing hot environments. Examples include fusion plasmas (Duxbury *et al* 1998, Brezinsek *et al* 2007, 2014), combustion (Linton and Broida 1977, Glumac *et al* 2001), laser ablation (Varenne *et al* 2000, Zhang and Li 2003, Kobayashi and Sekine 2006), laser-induced plasmas (Bai *et al* 2014, Surmick and Parigger 2014) and discharges (Vallon *et al* 2009, Chan *et al* 2013). Other uses include atmospheric studies (Johnson 1965, Gole and Kolb 1981, Knecht *et al* 1996), measuring the magnetic fields in cool stars and brown dwarfs (Johns-Krull *et al* 1999, Reiners and Basri 2006, Shulyak *et al* 2010), monitoring the state distribution of reaction products (Song *et al* 2004, Chang *et al* 2005) and products of chemical vapour deposition (Nozaki *et al* 2000). The issues discussed in this review are relevant also to calculations of collisions of open-shell atoms, though there are additional problems in these systems not covered in the current review.

Theoretically the study of rotationally and vibrationally resolved electronic (rovibronic) spectra of diatomics needs to consider couplings due to several sources of angular momentum such as electronic spin, electron orbital angular momentum and molecular rotational motion. To these can be added the hyperfine effects due to nuclear spin angular momentum and the possible effects of external fields. The various couplings are complicated compared to their atomic equivalents by the presence of the nuclear axis. These problems have been considered over many years and have been the subject of a number of books (Herzberg 1950, Kovács 1969, Mizushima 1975, Lefebvre-Brion and Field 1986, 2004, Brown and Carrington 2010). However the approach encapsulated in these works involves the extensive use of perturbation theory to treat the various angular momentum couplings and, often, other aspects of the problem too. Whereas such approaches have proved effective for parameterising experimental data, they are problematic when the couplings are strong; in such difficult cases the couplings may be ascribed to the wrong physical mechanism (McKemmish *et al* 2016b). Even vibronic assignment of experimental spectra using these approaches remains questionable (Yurchenko *et al* 2016a). Furthermore, use of perturbation theory to treat the couplings is less useful for formulating predictive, first principles studies.

Particularly challenging is the treatment of diatomic molecules containing at least one transition metal atom. These systems often have several low-lying electronic states, which is why they are important astronomically, and have a complicated electronic structure. We are participating in a project called ExoMol which is aimed at computing line lists for all molecular species important in hot astronomical atmospheres, such as those found around cool stars, brown dwarfs and exoplanets (Tennyson and Yurchenko 2012). As part of this project it was necessary to consider extensive rovibronic spectra of a variety of closed shell (Barton *et al* 2013, 2014, Yorke *et al* 2014, Paulose *et al* 2015, Rivlin *et al* 2015) and open shell (Yadin *et al* 2012, Lodi *et al* 2015, Patrascu *et al* 2015, Tennyson *et al* 2016b, Yurchenko *et al* 2016a) diatomics. Studies on some of the simpler systems have used perturbation theory to include the effects of fine structure (Yadin *et al* 2012, Tennyson *et al* 2016b); similar methods have been used by other groups studying diatomics composed of light atoms (Brooke *et al* 2013, Hinkle *et al* 2013, Brooke *et al* 2014a, 2014b, Ram and Brooke 2014, Brooke *et al* 2016). However, the complexity of open shell transition metal diatomics (often combined with a shortage of experimental data) means that their spectra may not be well-treated by this approach. This has led us to develop a procedure for the direct solution of the Schrödinger equation augmented with coupling terms, such as spin–orbit coupling, which arise from the inclusion of relativistic effects in the problem (Patrascu *et al* 2014, Lodi *et al* 2015). It is these procedures, and related work performed by other groups, that concern us here. Early work in this direction was performed by Marian (Marian 1995, 2001) who calls this a matrix procedure because, as we shall see, it is based on the construction and diagonalisation of matrices involving the nuclear motion wavefunctions of several electronic states to give energy levels and associated fully coupled wavefunctions.

There are well developed programs for solving the uncoupled diatomic nuclear motion problem such as LEVEL (Le Roy 2007). Although there are a growing number of studies treating coupled electronic states (Carrington *et al* 1995, Tamanis *et al* 2002, Bergeman *et al* 2003, Meshkov *et al* 2005, Hutson and Tiesinga 2008, Zhang *et al* 2010, Gopakumar *et al* 2013, Brooke *et al* 2014b), there appears to be a lack of general programs for the solving the matrix procedure. We note BOUND by Hutson (1994) can be used in this fashion. Recently we have developed a program, DUO, to solve the general, coupled-states diatomic nuclear motion problem (Yurchenko *et al* 2016b).

Modern electronic structure theory is generally able to reproduce the basic properties of the potential energy surfaces of open shell diatomics made up by main group, light atoms (H to Ar). Generally speaking because of inevitable computational limitations the accuracy obtainable by electronic structure theory decreases as the number of electrons in the molecule increases. For example, the excitation energies, vibrational frequencies and bond lengths of complicated open shell systems such as C_2 are well reproduced by theory (Schmidt and Bacskay 2007, 2011, Nakajima *et al* 2009).

The situation is rather worse when we consider transition metal diatomics. In these cases not only does one have to deal with an increased number of electrons but also the density of electronic states is higher, leading to more frequent perturbations. In this review, we concentrate on these cases as they represent the most challenging situations, specifically from the perspective of electronic structure theory.

Table 1. Summary of the notation used for angular momenta in diatomic molecules after Lefebvre-Brion and Field (1986).

Angular momentum	Operator	Projection[a]	Commutation[b]
Electronic orbital	$\hat{\mathbf{L}} = \sum_i \hat{\mathbf{l}}_i$	Λ	Normal
Electron spin	$\hat{\mathbf{S}} = \sum_i \hat{\mathbf{s}}_i$	$M_S = \Sigma$	Normal
Total electronic	$\hat{\mathbf{J}}_a = \hat{\mathbf{L}} + \hat{\mathbf{S}}$	$\Omega = \Lambda + \Sigma$	Normal
Nuclear rotational	$\hat{\mathbf{R}}$	0	Anomalous
Nuclear spin	$\hat{\mathbf{I}} = \hat{\mathbf{I}}_a + \hat{\mathbf{I}}_b$	$M_I = \Omega_I$	Normal
Nuclear rotational plus electronic orbital	$\hat{\mathbf{N}} = \hat{\mathbf{R}} + \hat{\mathbf{L}}$	$M_N = \Lambda$	Anomalous
Nuclear rotational plus electron spin	$\hat{\mathbf{O}} = \hat{\mathbf{R}} + \hat{\mathbf{S}}$	Σ	Anomalous
Nuclear rotational plus total electronic	$\hat{\mathbf{J}} = \hat{\mathbf{R}} + \hat{\mathbf{L}} + \hat{\mathbf{S}}$	Ω	Anomalous
'Total' angular momentum	$\mathbf{F} = \hat{\mathbf{R}} + \hat{\mathbf{L}} + \hat{\mathbf{S}} + \hat{\mathbf{I}}$	Ω_F	Anomalous

[a] Label used for the z axis (i.e., the internuclear vector).

[b] Whether the components of the given angular momentum along the body-fixed axes obey normal ($[A_x, A_y] = \mathrm{i}\hbar A_z$) or anomalous ($[A_x, A_y] = -\mathrm{i}\hbar A_z$) commutation relations.

2. Overall method

When the diatomic molecule is not in a $^1\Sigma^\pm$ electronic state interactions between the various terms are present and one cannot treat each electronic state in isolation.

The procedure followed starts by making the Born–Oppenheimer approximation and separating the electronic and nuclear motion, although it is possible to partially correct for this approximation later in the calculation. Consideration of relativistic and other angular momentum effects leads to couplings which are considered in detail in the next section. The resulting nuclear motion Hamiltonian appears quite complicated but is amenable to direct variational solution (Yurchenko *et al* 2016b). However, the calculation of the necessary potential energy curves (PECs) and angular momentum coupling curves remains challenging.

In particular, as discussed in more detail in section 3, there are three main sources of angular momentum: electronic orbital angular momentum $\hat{\mathbf{L}}$, electronic spin angular momentum $\hat{\mathbf{S}}$, and nuclear rotation angular momentum $\hat{\mathbf{R}}$; in turn, these lead to a multitude of interactions (couplings) between different electronic states. These angular momenta should be coupled together to form the total angular momentum $\hat{\mathbf{J}}$, which is the only conserved angular momentum in the system. For three angular momentum operators there are in principle $3! = 6$ possible ordering, and these orderings are generally denoted Hund's cases and labelled with the letters (*a*), (*b*), (*c*), (*d*), (*e*), and (*e*′) (Stepanov and Zhilinksii 1974, Nikitin and Zare 1994, Brown and Carrington 2010). For perturbative treatments the order in which these couplings are performed matters. In treatments which aim at a full solution of the problem they just represent how the angular basis set is constructed and, given a complete basis, the results should be independent of this choice. Formal issues arising from the open shell diatomic problem have recently been discussed in detail by Schwenke (2015), who like us and Marian (1995), favours the use of a Hund's case (*a*) representation of the problem. In this scheme the problem is represented in terms of the angular momenta J and R, and the projections along the molecule's internuclear axis, Λ, Σ and Ω, see table 1. Of these only J and the parity are actually conserved quantities.

Dipole moment curves (DMCs), both diagonal and between different states, are required to give transition probabilities. The accurate calculation of these various curves requires solution of electronic structure problems which remain challenging in the presence of a transition metal atom. These are discussed in section 4.6.

3. Formal considerations

3.1. Body-fixed Hamiltonian for diatomics

The non-relativistic Hamiltonian in the absence of external fields of a diatomic molecule with nuclei A and B and n electrons is given by:

$$\begin{aligned}\hat{H} &= \hat{T}_{\mathrm{N}} + \hat{T}_{\mathrm{e}} + V_{\mathrm{NN}} + V_{\mathrm{ee}} + V_{\mathrm{Ne}} \\ &= -\frac{\hbar^2}{2M_A}\vec{\nabla}_A^2 - \frac{\hbar^2}{2M_B}\vec{\nabla}_B^2 + \frac{\hbar^2}{2m_{\mathrm{e}}}\sum_{i=1}^{n}\vec{\nabla}_i^2 \\ &\quad + \frac{1}{4\pi\varepsilon_0}\left\{\frac{Z_A Z_B}{|\mathbf{R}_A - \mathbf{R}_B|} + \sum_{i<j}^{n}\frac{q^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i=1}^{n}\left[\frac{Z_A q}{|\mathbf{r}_i - \mathbf{R}_A|}\right.\right. \\ &\quad \left.\left. + \frac{Z_B q}{|\mathbf{r}_i - \mathbf{R}_B|}\right]\right\},\end{aligned} \tag{1}$$

where nucleus I ($I = A, B$) has mass M_I, charge Z_I and is represented by coordinate $\mathbf{R}_I$; q is the elementary positive charge; the electrons are represented by coordinates $\mathbf{r}_i$. We will call the Cartesian coordinates defining the Hamiltonian above *laboratory-fixed*.

The Hamiltonian (1) has the following exact symmetries (Lodi and Tennyson 2010):

(i) It is invariant to rigid translations of all coordinates.
(ii) It is invariant to rigid rotation of all coordinates.
(iii) It is invariant to inversion of all coordinates.

(iv) It is invariant to permutation of any two electronic coordinates.
(v) If the two nuclei are identical, it is invariant to permutation of the nuclear coordinates.

Symmetry (i) implies that the centre-of-mass motion of the system can be separated out. Symmetry (ii) that the sum of orbital and rotational angular momenta, $\hat{\mathbf{N}}$, is a conserved quantity; furthermore the state is $N(N+1)$ times degenerate and one may refer to one specific degenerate component by specifying the projection of $\hat{\mathbf{N}}$ along the laboratory Z axis, M_N. Symmetry (iii) indicates that parity $\tau = \pm 1$ is a conserved quantity and can be used as a quantum number, for which the label e or f are generally used (Brown *et al* 1975). Symmetry (iv) merely indicates that we can always satisfy the Pauli principle (i.e., we can always choose a solution antisymmetric with respect to exchange of any two electron coordinates). Similarly for symmetry (v), if the two nuclei are identical, we can always find a solution which is antisymmetric or symmetric with respect to nuclear interchange; this gives rise to the well-known ortho and para states of homonuclear diatomics (Bunker and Jensen 1998).

Hamiltonian (1) is non-relativistic so commutes with the electron and nuclear spin operators $\hat{\mathbf{S}}$ and $\hat{\mathbf{I}}$ as well as their projections along the laboratory Z axis, so that a wave function has a degree of degeneracy equal to $N(N+1)\,S(S+1)\,I\,(I+1)$. One can refer to specific degenerate components by specifying the quantum numbers of the projection operators along the laboratory Z axis, M_N, M_S and M_I, or alternatively by specifying the total angular momentum $\hat{\mathbf{F}} = \hat{\mathbf{N}} + \hat{\mathbf{S}} + \hat{\mathbf{I}}$ and its component along the laboratory Z axis, M_F. In summary, Hamiltonian (1) admits the following exact quantum numbers: N and M_N (overall angular momentum of all particules excluding spin and its projection); τ (inversion parity quantum number); S and M_S (electron spin quantum number and its projection); I and I_S (nuclear spin quantum number and its projection). We note that similar considerations hold for any molecule, not just diatomics. Any other label used specifically for diatomics, such as Λ, must therefore be considered an approximate quantum number.

Details on how to separate the translational and rotational degrees of freedom can be found elsewhere (Kolos and Wolniewicz 1963, Bunker 1968, Pack and Hirschfelder 1968, Judd 1975, Sutcliffe 2007, Islampour and Miralinaghi 2015). It is customary for diatomics to choose body-fixed coordinates such that the origin is at the centre of nuclear mass and the body-fixed z axis always points along the internuclear vector. If one deals with the rotational symmetry by introducing new, rotationally invariant ('body-fixed') coordinates and integrating out the degrees of freedom corresponding to the rotational symmetry (Pack and Hirschfelder 1968, Hornkohl and Parigger 1996, Sutcliffe 2007, Islampour and Miralinaghi 2015), then one obtains an effective Hamiltonian depending on two quantum numbers, namely the total angular momentum J and its projection along the body-fixed z axis, Ω. The effective Hamiltonian one obtains is (see equation (12) of Bunker 1968) is:

$$\hat{H}_{\mathrm{eff}} = \hat{H}_{\mathrm{e}} + \hat{H}_{\mathrm{v}} + \hat{H}_{\mathrm{R}} + \hat{H}_{\mu}, \tag{2}$$

where $\hat{H}_{\mathrm{e}}$ is the electronic Hamiltonian and is given by

$$\hat{H}_{\mathrm{e}} = \hat{T}_{\mathrm{e}} + V_{\mathrm{NN}} + V_{\mathrm{ee}} + V_{\mathrm{Ne}} \tag{3}$$

and the terms are defined in Hamiltonian (1). The body-fixed vibrational energy operator $\hat{H}_{\mathrm{v}}$ is

$$\hat{H}_{\mathrm{v}} = -\frac{\hbar^2}{2\mu}\frac{1}{R}\frac{\partial^2}{\partial R^2}R, \tag{4}$$

where R is the internuclear separation and

$$\mu = \left(\frac{1}{M_A} + \frac{1}{M_B}\right)^{-1} \tag{5}$$

is the reduced mass of the molecule. Note that if, as is customary, a factor $1/R$ is included in the definition of the vibrational wavefunction $\phi(R)$:

$$\phi(R) = u(R)/R \tag{6}$$

then if we choose to work with the wavefunction $u(R)$ the body-fixed vibrational energy operator $\hat{H}_{\mathrm{v}}$ takes on the simpler form

$$\hat{H}_{\mathrm{v}} = -\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial R^2}. \tag{7}$$

The body-fixed coordinate rotational energy operator $\hat{H}_{\mathrm{R}}$ is given by

$$\hat{H}_{\mathrm{R}} = B\,\hat{\mathbf{R}}^2, \tag{8}$$

where $B = \hbar^2/(2\mu R^2)$, and $\hat{\mathbf{R}}$ is the body-fixed rotational angular momentum; finally, $\hat{H}_{\mu}$ is the mass-polarisation energy given by

$$\hat{H}_{\mu} = -\frac{\hbar^2}{8\mu}\sum_{i=1}^{N}\sum_{j=1}^{n}\vec{\nabla}_i \cdot \vec{\nabla}_j \tag{9}$$

The mass polarisation term is small and can safely be neglected in all but the highest accuracy calculations (Kutzelnigg 1997).

Effects due to couplings between the electronic PECs of $\hat{H}_{\mathrm{v}}$ and of the diagonal part of $\hat{H}_{\mathrm{R}}$ are generally referred to as non-adiabatic and their inclusion is important in high-accuracy studies. While treatment of the electronically diagonal adiabatic correction is relatively straightforward *ab initio* (Handy *et al* 1986, Dinelli *et al* 1995, Kutzelnigg 1997), inclusion of the non-adiabatic effects is not. The relative importance of the adiabatic versus non-adiabatic correction terms is considered by Reimers *et al* (2015). There have been some attempts to treat non-adiabatic effects in a completely *ab initio* fashion starting from the classic works on H_2 by Kolos and Wolniewicz (1963); other early studies include those by Herman and Asgharian (1968), Bunker and Moss (1977) and Hutson and Howard (1980). Work on non-Born–Oppenheimer effects for H_2 continues (Pachucki and Komasa 2014) and, indeed, has reached the exquisite accuracy of of 10^{-4} cm^{-1} for the vibrational fundamentals of the

Table 2. Coupling rules for matrix elements of the body-fixed Hamiltonian given by equation (2) using the (non-symmetrised) basis functions of equation (12). The coupling rules $\Delta J = 0$ and $g \nleftrightarrow u$ (only for homonuclear diatomics) always hold. For the symmetrised basis functions given by equation (16) there is a further universal selection rule, namely $e \leftrightarrow e$ and $f \leftrightarrow f$ are possible but not $e \leftrightarrow f$.

		Coupling rules				
Description	Equation[a]	$\lvert\Delta S\rvert$	$\lvert\Delta\Sigma\rvert$	$\lvert\Delta\Lambda\rvert$	$\lvert\Delta\Omega\rvert$	Notes
Vibrational and non-adiabatic, $\hat{H}_v$	(14)	0	0	0	0	b
Rotational diagonal	(18)	0	0	0	0	
S-uncoupling, $\hat{J}_\pm\hat{S}_\mp$	(19)	0	1	0	1	
L-uncoupling, $\hat{J}_\pm\hat{L}_\mp$	(20)	0	0	1	1	
Spin-electronic, $\hat{L}_\pm\hat{S}_\mp$	(21)	0	1	1	0	
Spin–orbit, $\hat{H}_{SO}$	c	0,1	0, 1	0, 1	0	d, e
Spin-rotation, $\hat{H}_{SR}$	c	0	1	0	1	
Spin–spin, $\hat{H}_{SS}$	c	0,1,2	0,1,2	0,1,2	0	f, g

[a] Relevant equation in the text defining the operator.

[b] Matrix elements of $\hat{H}_v$ between different electronic states (having the same molecular term symbol) are considered non-adiabatic interactions.

[c] See chapter 3 of Brown and Carrington (2010).

[d] Extra selection rule for Σ electronic states: $\Sigma^\pm \leftrightarrow \Sigma^\mp$ but $\Sigma^\pm \nleftrightarrow \Sigma^\pm$.

[e] The matrix element is zero if $\Delta S = 0$ and $\Sigma' = \Sigma'' = 0$.

[f] Extra selection rule for Σ electronic states: $\Sigma^\pm \leftrightarrow \Sigma^\pm$ but $\Sigma^\pm \nleftrightarrow \Sigma^\mp$; the converse of that for $\hat{H}_{SO}$, see note d.

[g] Spin–spin interaction is zero between Σ states with $S \leqslant 1/2$.

main isotopologues (Dickenson *et al* 2013). Schwenke (2001) proposed a more general method of treating non-adiabatic effects in molecules which he tested on H_2^+. In practical application of these approaches, e.g. by Le Roy and Huang (2002), non-adiabatic effects are taken into account by replacing the rotational kinetic energy expression in equation (8) by

$$\frac{\hbar^2}{2\mu R^2} \rightarrow \frac{\hbar^2}{2\mu R^2}[1 + \alpha(R)], \tag{10}$$

and the vibrational kinetic energy operator in equation (7) by

$$\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial R^2} \rightarrow \frac{\hbar^2}{2\mu}\frac{\partial}{\partial R}[1 + \beta(R)]\frac{\partial}{\partial R}, \tag{11}$$

where the unitless functions $\alpha(r)$ and $\beta(r)$ (sometimes called the rotational/vibrational Born–Oppenheimer breakdown function or the rotational/vibrational g factors) are obtained either semi-empirically by fitting to experimental data from more than one isotope or by *ab initio* means (Sauer 1998, Bak *et al* 2005). However, as discussed under inverse problems below, Watson (2004) noted that experimental data alone are not generally enough to fully determine the α and β functions.

This approach of Le Roy and Huang is ultimately based on a perturbative treatment of non-adiabatic effects and may break down in presence of avoided crossings between the PECs. In such cases it is usually preferable to explicitly treat the off-diagonal matrix elements of the kinetic energy operator (4) which can be done by borrowing approaches originally developed to describe scattering processes (Hutson 1994). Alternatively, but possibly equivalently, one can introduce diabatic (crossing) curves (Lewis and Hougen 1968), as done, for example, in a recent study on C_2 (Kokkin *et al* 2007).

To the non-relativistic laboratory-fixed Hamiltonian (1) one can also add further interaction terms, see, e.g., chapter 3 of Brown and Carrington (2010) for a derivation and list of interactions. In particular, the spin–orbit Hamiltonian operator is usually essential for even qualitative accuracy of transition-metal-diatomic spectra while the spin-rotation and spin–spin operators are sometimes important in high accuracy studies. The coupling rules which govern the interactions between these terms are given in table 2.

In principle, these terms can be evaluated once the spin is included into the wavefunction. However, only the spin–orbit matrix elements are routinely computed within specialised electronic structure programs. The one-electron component of the spin–orbit coupling usually dominates; therefore, treatment of electron correlation is less critical than for other properties (Lischka *et al* 2011). For the other spin-terms, we in practice often use effective coupling terms for the spin–spin and spin-rotational Hamiltonian operators and fit to experimental energies or frequencies. These are discussed in more detail by Yurchenko *et al* (2016).

3.2. Wavefunctions

Within a Hund's case (a) frawework, a complete basis set can be constructed by multiplying the electronic wave functions by a set of functions complete for the nuclear (vibrational and rotational) degrees of freedom, giving:

$$\begin{aligned}&|\text{state}, J, \Omega, \Lambda, S, \Sigma, v\rangle \\ &= |\text{state}, \Lambda, S, \Sigma\rangle |J, \Omega, M\rangle |\text{state}, J, S, \Lambda, \Omega, v\rangle,\end{aligned} \tag{12}$$

where (see also table 1) $\Lambda = 0, \pm 1, \pm 2, \ldots$is the eigenvalue of $\hat{L}_z$; S is the electron spin quantum number; M is the projection of the total angular momentum along the laboratory axis Z; v is the vibrational quantum number. For the rovibronic basis set the combinations of Σ and Λ are selected to satisfy $-J \leqslant \Omega \leqslant J$. The label 'state' is a counter over electronic states having the same symmetry. The $|\mathrm{state}, \Lambda, S, \Sigma\rangle$ are solutions of the electronic structure problem and can be obtained (although usually not exploiting the full $C_{\infty v}$ or $D_{\infty h}$ point-group symmetry of a diatomic system) using a number of electronic structure packages; the $|J, \Omega, M\rangle$ are symmetric top eigenfunctions which are Wigner $\mathcal{D}$ functions (Pack and Hirschfelder 1968, Zare 1988, Sutcliffe 2007, Islampour and Miralinaghi 2015) and depend on the Euler angles (α, β, γ) specifying the orientation of the body-fixed axis with respect to the space-fixed one:

$$|J, \Omega, M\rangle = \sqrt{\frac{2J+1}{4\pi}} \mathcal{D}^{J}_{M,\Omega}\left(\alpha, \beta, \gamma = \frac{\pi}{2}\right)^{*}. \quad (13)$$

Note that in the expression above the third Euler angle, γ, has been fixed to the value $\pi/2$ as the condition that the body-fixed z axis points from one nucleus to the other leaves it completely unconstrained; the normalisation factor has been chosen so that that no integration over γ should be performed. This is the customary choice for diatomics (Vleck 1951), although other treatments of γ are possible (Judd 1975, Hornkohl and Parigger 1996).

Finally, $|\mathrm{state}, J, S, \Lambda, \Omega, v\rangle$ are vibrational functions found as solutions of the one-dimensional Schrödinger equations for the electronic potential curves $E_n(r)$ (possibly complemented by the diagonal part of the rotational Hamiltonian, equation (22)) and will be discussed in detail in the next section.

Note that our notation implies that the electronic wave functions $|\mathrm{state}, \Lambda, S, \Sigma\rangle$ are chosen such that:

$$\langle \mathrm{state}, \Lambda, S, \Sigma|\hat{L}_z|\mathrm{state}, \Lambda, S, \Sigma\rangle = \Lambda, \quad (14)$$

$$\hat{\sigma}_v(xz)|\mathrm{state}, \Lambda, S, \Sigma\rangle = (-1)^{s_q+\Lambda+S-\Sigma}|\mathrm{state}, -\Lambda, S, -\Sigma\rangle, \quad (15)$$

where $\hat{\sigma}_v(xz)$ is the operator corresponding to reflection through the body-fixed xz-plane and where $s_q = 1$ for Σ^- electronic states and $s_q = 0$ in all other cases; commonly used quantum chemistry programs such as Molpro (Werner *et al* 2012) do not use this form and therefore couplings obtained from such programs need to be converted (Patrascu *et al* 2014, Schwenke 2015, Yurchenko *et al* 2016b).

As a second and final step one computes the matrix elements of the Hamiltonian (2) (plus, if desired, any other additional Hamiltonian components such as spin–orbit coupling, spin-rotation interaction etc) in the chosen basis set and obtains the final energies and wave functions by diagonalisation of the Hamiltonian matrix.

The exact wave function has a definite parity with respect to inversion of all laboratory-fixed coordinates; on the other hand the basis functions given of equation (12) do not. Laboratory-fixed inversion is equivalent to reflection through the molecule-fixed xz plane (Pack and Hirschfelder 1968, Røeggen 1971, Kato 1993). Symmetrised basis functions having definite parity $\tau = \pm 1$ are given by

$$\begin{aligned}&|\mathrm{state}, J, |\Omega|, |\Lambda|, S, |\Sigma|, v, \tau\rangle\\ &= \frac{1}{\sqrt{2}}(|\mathrm{state}, J, \Omega, \Lambda, S, \Sigma, v\rangle\\ &\quad + \tau(-1)^{s_q+J-S}|\mathrm{state}, J, -\Omega, -\Lambda, S, -\Sigma, v\rangle).\end{aligned} \quad (16)$$

This parity relates to the standard linear-molecule e/f parity labels (Brown *et al* 1975) as follows. For Bosons (J integer) e states have parity given by $(-1)^J$ and f states by $(-1)^{(J+1)}$; for Fermions this becomes $(-1)^{(J-\frac{1}{2})}$ for e states and $(-1)^{(J+\frac{1}{2})}$ for f states.

3.3. Rotational couplings

Actual calculations require matrix elements of the effective Hamiltonian (2). In the basis set functions given by equation (12), the rotational angular momentum $\hat{\mathbf{R}}$ appearing in equation (8) can be expanded as (see table 1)

$$\hat{\mathbf{R}} = \hat{\mathbf{J}} - \hat{\mathbf{L}} - \hat{\mathbf{S}}. \quad (17)$$

The rotational Hamiltonian given by equation (8) can be written as (Lefebvre-Brion and Field 1986)

$$\hat{H}_{\mathrm{R}} = \frac{\hbar^2}{2\mu r^2}\{(\hat{J}^2 - \hat{J}_z^2) + (\hat{S}^2 - \hat{S}_z^2) + (\hat{L}^2 - \hat{L}_z^2) \quad (18)$$

$$+(\hat{J}_+\hat{S}_- + \hat{J}_-\hat{S}_+) \quad (19)$$

$$-(\hat{J}_+\hat{L}_- + \hat{J}_-\hat{L}_+) \quad (20)$$

$$+(\hat{L}_+\hat{S}_- + \hat{L}_-\hat{S}_+)\}. \quad (21)$$

The second term in $\hat{H}_{\mathrm{R}}$ (equation (19)) is due to terms of the type $\hat{J}_\pm\hat{S}_\mp$ and is called spin uncoupling, see, for example page 626 of Brown and Carrington (2010) for a description. The third term in $\hat{H}_{\mathrm{R}}$ (equation (20)) is due to terms of the type $\hat{J}_\pm\hat{L}_\mp$ and is called L-uncoupling. This term is responsible for the Λ-doubling of Π, Δ, Φ states (i.e., the splitting of the $\tau = +$ and $\tau = -$ components of non-Σ states). The fourth term in $\hat{H}_{\mathrm{R}}$ (equation (21)) is due to terms of the type $\hat{L}_\pm\hat{S}_\mp$ is a spin-electronic term which obeys coupling rules very similar to the spin–orbit Hamiltonian and hence experimentally it cannot generally be distinguished from spin–orbit interactions.

Matrix elements of the rotational Hamiltonian (18)–(21) in the basis given by equation (12) can be evaluated using the rules of the angular momentum (Lefebvre-Brion and Field 1986). The coupling rules for the rotational Hamiltonian, as well as for other components of the total Hamiltonian (2) (spin–orbit, spin-rotation and spin–spin interactions) are given in table 2.

The expectation value of the first term in $\hat{H}_{\mathrm{R}}$, equation (18), for each of the basis functions (12) gives rise to the well-known rotational centrifugal potential. Its effect amounts to an additive potential term to the Born–Oppenheimer potential which can be written in the following equivalent ways:

$$
\begin{aligned}
H_{\mathrm{R}}^{\mathrm{diag}}
&= \langle J,\,\Omega,\,M|\,\langle \mathrm{state},\,\Lambda,\,S,\,\Sigma|\hat{H}_{\mathrm{R}}|\mathrm{state},\,\Lambda,\,S,\,\Sigma\rangle\,|J,\,\Omega,\,M\rangle\\
&= B\big[[J(J+1)-\Omega^2]+\big[S(S+1)-\Sigma^2\big]\\
&\quad + L_x^2 + L_y^2 - \Lambda^2\big]\\
&= B[J(J+1)+S(S+1)-2(\Lambda^2+\Lambda\Sigma+\Sigma^2)\\
&\quad + L_x^2 + L_y^2]\\
&= B[J(J+1)+S(S+1)-2\Omega(\Lambda+\Omega)+L_x^2+L_y^2].
\end{aligned}
\tag{22}
$$

For $^1\Sigma$ states the expression above reduces to the well-known expression $BJ(J+1)$. In the absence of $H_{\mathrm{R}}^{\mathrm{diag}}$ the non-relativistic wavefunctions are 2 $(2S+1)$-times degenerate for $\Lambda \neq 0$ and $(2S+1)$-times for $\Lambda = 0$. Inclusion of $H_{\mathrm{R}}^{\mathrm{diag}}$ partially splits these degenerate components according to their value of Λ and Σ. Specifically, for $S < \lfloor \Lambda/2 \rfloor$ each state splits by effect of $H_{\mathrm{R}}^{\mathrm{diag}}$ in $2S+1$ components, while for $S \geqslant \lfloor \Lambda/2 \rfloor$ each state splits into $\lfloor S + \Lambda/2 + 1 \rfloor$ components, where $\lfloor x \rfloor$ indicates the floor function, i.e. the largest integer not greater than x. In *ab initio* treatments L_x^2 and L_y^2 are functions of R obtained by averaging the body-fixed angular momentum operators over the electronic wave function. Essentially they amount to a small correction to the Born–Oppenheimer potential $V(R)$ and in experimental analyses they are not considered separately from it. Because of the cylindrical symmetry of the electronic problem $L_x(R) = L_y(R)$. Note that the values of L_x and L_y depend on the choice of the origin of the body-fixed axes, and for consistency with the rest of the treatment, we recommend that they are computed with the origin fixed at the centre of nuclear mass. Because of this choice of the origin upon dissociation $L_x(R)$ and $L_y(R)$ grow proportionally to R, and the term $B(L_x^2 + L_y^2)$ in equation (22) tends to a constant value as $B \propto 1/R^2$.

4. Electronic structure calculations

4.1. Overview

The above formalism is largely concerned with the couplings of the various angular momenta and is, in principle, exact. The largest source of uncertainty in computing the energy levels arises from solution of the electronic structure problem to give the required PECs and couplings between electronic states, specifically the spin–orbit coupling and L-uncoupling matrix elements. At the moment only a few electronic structure packages, such as Dalton (Aidas *et al* 2014), are capable of computing the spin-rotation and spin–spin matrix elements and such terms are usually dealt with empirically.

Ab initio electronic structure theory has been used to predict the properties of many electronic states in diatomics containing one transition metal. There are many recent examples of such calculations (Kalemos and Mavridis 2000, Borin and de Macedo 2004, Abdul-Al *et al* 2005, Midda *et al* 2006, Ramírez-Solís 2006, Tzeli and Mavridis 2006, Demovič 2007, Ghanmi *et al* 2007, Koukounas and Mavridis 2008, Ribas *et al* 2008, Kardahakis and Mavridis 2009, Miliordos and Mavridis 2010, Sakellaris *et al* 2010, Goel and Masunov 2011, Papakondylis 2011, Sakellaris *et al* 2011, Shi *et al* 2011, DeYonker and Allen 2012, Kaplan and Miranda 2012, Sakellaris and Mavridis 2012a, 2012b, 2013, Borin *et al* 2014, DeYonker *et al* 2014, Karman *et al* 2014, Karman and Groenenboom 2014, Shi *et al* 2015). There has also been investigations into using *ab initio* electronic structure theory to study the even more complicated problem of electronic states in diatomics containing two transition metals (Czuchaj *et al* 1997, Gao *et al* 2006, Zhang *et al* 2007, Gao *et al* 2009, Camacho *et al* 2010, Kalemos *et al* 2010, Kalemos and Mavridis 2011, Krechkivska *et al* 2012, Coe *et al* 2014, Kaplan and Miranda 2014, Kalemos 2015, Kalemos *et al* 2015). For example, the ground electronic state of the chromium dimer, Cr_2, is a remarkably challenging system and is often used as a benchmark to test new theoretical methods (Müller 2009, Kurashige and Yanai 2011, Sokolov and Chan 2016).

If one wants to predict or model to the highest possible accuracy the rovibronic spectroscopy of transition metal diatomics it is usually imperative to use multireference wavefunction-based methodologies which are able to treat both the so-called static and dynamic parts of electron correlation, see the review by Szalay *et al* (2012) for a general discussion. These approaches generally take as a starting point a multireference self-consistent field wave function, very often of the complete active space (CASSCF) type (Roos and Taylor 1980, Olsen 2011), and improve upon it using either perturbation theory or diagonalisation of an opportune, reduced-size Hamiltonian matrix. Methods bases on perturbation theory include the popular CASPT2 method (Andersson *et al* 1990, 1992), the n-electron valence state perturbation theory method (Angeli *et al* 2001, 2007), as well as others (Werner 1996, Celani and Werner 2000, Kállay 2015), while methods based on diagonalisation include internally contracted multireference configuration interaction (icMRCI) (Szalay *et al* 2012) and closely related modifications such as averaged coupled pair functional (ACPF) (Gdanitz and Ahlrichs 1988) and averaged quadratic coupled cluster (AQCC) (Szalay and Bartlett 1995, Szalay 2008). Among electronic structure methods which are generally applicable both to the ground as well as to excited electronic states (also for highly stretched geometries) icMRCI-type ones are the most accurate, and in the following sections we will deal solely with them. In the remainder of the present section we briefly discuss some other alternatives.

Among single-reference electronic structure methods, i.e. methods which take as a starting point a Hartree–Fock type wavefunction, the most successful and widely applied is probably the CC method, (Bartlett and Musiał, 2007), especially in its (closed-shell) CCSD(T) version (Raghavachari *et al* 1989). CC methods are generally used to compute properties of the ground electronic state of closed-shell systems close to equilibrium, and when one of these three qualifications is violated complications arise. For example, CC approaches for open-shell system do exists but are much less developed (Knowles *et al* 1993, 2000, Watts *et al* 1993) and may not give access to all possible values of spin or symmetries. For highly stretched geometries CC methods are inevitably expected to degrade very significantly in quality or even to break down, so that complete energy curves up to dissociation cannot in general be computed. Multireference generalization of coupled-cluster are being developed but at the moment they are not in widespread use nor they can provide better accuracy than icMRCI-type ones (Szalay 2010, Lyakh 2011, Rolik and Kállay 2014).

Finally, a comment is warranted on density functional theory (DFT) methods, which have proved very successful in applications to main group species and material science. The DFT methodology is based on the choice of an exchange and correlation functional, and a functional appropriate for transition metal system has proved difficult to obtain and, despite recent progress in this direction (Zhao and Truhlar 2008, Cramer and Truhlar 2009, Cohen *et al* 2012), DFT methods are currently incapable of providing the necessary accuracy for high-resolution electronic spectroscopy of transition metal diatomics.

4.2. Computational considerations

It may be thought that for such small (two atom) systems calculation time is not a problem and that most *ab initio* quantum chemistry methods are practical; however, this is definitely not the case. Some methodology changes have practically no influence on calculation time, e.g. inclusion of *a posteriori* size-consistency corrections such as the Davidson correction (+Q) (Langhoff and Davidson 1974, Szalay *et al* 2012) and relativistic corrections using the mass-velocity and Darwin terms. Diagonal and parallel off-diagonal finite field dipole moment calculations increase calculation time by up to a factor of three. Changes to the way in which the complete active space self-consistent field (CASSCF) orbitals are optimised can cause or alleviate convergence problems, but otherwise have little impact on calculation time. Increases to the basis set size have a significant effect on calculation time; however, it is normally practical to perform calculations for diatomic systems with basis sets with sizes similar to the aug-cc-pVQZ basis set from the Dunning correlation-consistent family (Dunning 1989, Balabanov and Peterson 2005). The use of effective core potentials is a possible choice instead of all electron atomic basis sets. However, since we are mostly considering relatively light transition metals species with modest relativistic effects, we do not consider effective core potentials in detail here. Readers are invited to look at the recent review (Dolg and Cao 2012) for further discussion. Basis set superposition errors is also a consideration, particularly for calculating dissociation energies. However, in practice, other sources of error are found to be dominant, particularly when large basis sets are used. Furthermore, methods of addressing basis set superposition error are well established, for example, using standard counterpoise corrections.

There are also some improvements to methodology that pose such substantial increases to calculation time and memory requirements that they are often not practical for calculations along the full bond distance curve or for excited electronic states, though benchmark calculations at a single bond length may be feasible. Inclusion of semi-core correlation (e.g. including correlation from the 3s and 3p first-row transition metal electrons) falls into this category, especially when the main group element is heavier (e.g. oxygen, fluorine). Also, increases to the active space, such as including a second set of d orbitals, pose often insurmountable practical problems. This is unfortunate as both of these improvements would be highly desirable for transition metal systems.

As we shall see, current *ab initio* electronic structure calculations fail to achieve high accuracy for the spectroscopy of transition metal diatomics for some properties, particularly excitation energies. Therefore, fitting of PECs and other curves to experimental results is often used. However, these lower accuracy calculations can be used to demonstrate the complexity and nature of electronic states within a certain spectral band. For example, the study by Hübner *et al* (2015) of the excited states of VO demonstrates the density of doublet states within 20 000 cm^{-1} and 30 000 cm^{-1} is so high that correct modelling of small perturbations in the spectra of the $C^4\Sigma^-$ and $D^4\Pi$ state (origins at 17 420 cm^{-1} and 19 148 cm^{-1} respectively) is not currently feasible *ab initio*.

4.3. icMRCI orbitals and methodology

icMRCI calculations are far from straightforward and depend subtly on a number of key methodological parameters that are rarely explicitly discussed. We recommend a much more thorough specification of the methodological choices than is currently given; the standard brief description such as icMRCI/aug-cc-pVDZ is inadequate to allow reproducibility of the calculation.

icMRCI calculations use molecular orbitals that are usually derived from a CASSCF calculation. A CASSCF wavefunction is a linear combination of Slater determinants which all share a set of core doubly occupied orbitals and have variable occupation of a shared set of active orbitals. In a CASSCF calculation, these orbitals are optimised according to some criteria. For state-specific CASSCF, one electronic state with particular spin and symmetry is specified; the orbitals are optimised in order to minimise the energy of the CASSCF wavefunction of that state. During this process, both the orbitals themselves and the coefficients of each Slater determinant are optimised. For state-averaged (SA) CASSCF calculations, there are multiple CASSCF wavefunctions for each electronic state that share a single set of core and active orbitals, but vary in the coefficients of each Slater determinant. The orbitals and coefficients are all optimised to minimise the sum of the energy of the CASSCF wavefunctions for each state. It is also possible to put a weight on each state to preference optimisation of one electronic state over others. Though the CASSCF calculation produces energies, wavefunctions and other property evaluations for each component electronic state, none of this is used in the subsequent icMRCI calculation. The icMRCI calculation only uses the set of core, active and virtual orbitals produced during the CASSCF calculation (note the virtual orbitals are not occupied in any Slater determinant but are formed from orthogonal components of the atomic basis set). Only a single set of orbitals is produced regardless of the number of states involved in the CASSCF calculation. Thus, if one is interested in, say, the properties of state A, the inclusion of any other states in the CASSCF calculation will reduce the ability of the CASSCF orbitals to model the A state. Thus, icMRCI calculations using state-specific CASSCF orbitals should be better than icMRCI calculations using SA CASSCF orbitals; for example, the energy of the former should be lower than the latter, and thus closer to the true answer since icMRCI calculations are variational. The only exceptions to this are (1) accidental cancellation of errors can mean an inferior methodology happens to reproduce experiment more accurately and (2) the dynamic correlation is very strong and it happens that SA CASSCF orbitals can more accurately reproduce the dynamic correlation effects. Note that this latter case is not expected to arise very often and does not provide a justification for SA CASSCF calculations in general.

Despite the superiority of state-specific calculations from a theoretical perspective, there are a number of situations where one might require SA calculations, or where their use may be justified. First, it is imperative to include all lower-lying states of the same spin and symmetry in a CASSCF calculation. Second, currently there are no programs that allow computing spin–orbit matrix elements when the bra and ket do not originate from the same orthonormal set of CASSCF orbitals; in such cases it is therefore necessary to include both states in the optimisation of these orbitals. However, this is a limitation that could be addressed in future code development, and we would strongly endorse this.

In some cases, convergence can be improved by reducing symmetry from the linear point groups $C_{\infty v}$ and $D_{\infty h}$, which means further low-lying states of the same symmetry arise. Also, sometimes convergence is improved by including more states; though various arguments can be developed, this behaviour to our knowledge does not have a solid theoretical basis, but CASSCF calculations are notoriously troublesome and quirky in their convergence properties. Finally, SA calculations mean that all properties of a set of an electronic state can be determined together. This can be extremely helpful to ensuring the correct phase and relative signs of dipole moments, spin–orbit and electronic angular momentum matrix elements, particularly in a complex system (in this case, the absolute value of these matrix elements can be taken from icMRCI calculations using more accurate state-specific or minimal state CASSCF orbitals). Alternatively, sometimes SA calculations can be performed as a matter of convenience and reduced human effort and calculation time. However, we note that a single SA-CASSCF with many electronic states will almost certainly take longer than a single state-specific CASSCF. As we shall see, there are many sources of inaccuracy in current *ab initio* electronic structure theory calculations for transition metal diatomics and for many applications the error associated with state-averaging may not be important. However, in the latter case, we must caution that excessive consideration of other methodological choices, most notably basis set, are not justified. The errors associated with the use of double zeta basis set versus quadrupole zeta basis sets are found to be lower than the error associated with SA calculations.

Our experience (McKemmish *et al* 2016a) show that the effect of the choice of electronic states in the optimisation of the CASSCF orbitals can be large. However, we propose a standardised notation to describe the way in which the CASSCF orbitals for a particular icMRCI calculation are optimised. The states optimised in the CASSCF orbitals are put in brackets, separated by commas, then a dash followed by the words CAS are used. For example, (X, A)-CAS indicates CASSCF orbitals optimised for the X and A electronic states. If fractional weights are utilised, these are put before the state, e.g. (0.5 X, 1 A)-CAS.

Another often forgotten methodological consideration is that in internally contracted MRCI (Werner and Knowles 1988)—implemented in the popular package Molpro (Werner *et al* 2012)—the number of states requested in the icMRCI calculation affects the result. If more states are requested, less contraction occurs; this results in a longer calculation and lower absolute energies. We recommend that the number of states requested in the icMRCI calculation be denoted in brackets after the icMRCI; e.g. icMRCI(2) indicates a icMRCI calculation where 2 states were requested. More complicated notation (e.g. icMRCI(2, 1, 1, 2)) could be used to denote multiple states of different spin/symmetries. Rather than explicitly prescribing this more complicated notation here, we recommend describing the notation within the paper itself and ensuring that the point group, symmetry and spin of states are fully specified. Even better to ensure reproducibility of results, we encourage authors to provide sample input files to the electronic structure program used.

4.4. Correct identification of electronic state

The high density of electronic states for transition metal diatomics and the relative high inaccuracies in excitation energies (see below) makes the correct identification of electronic states in a calculation imperative, particularly when comparing against experiment and between different calculations. Particularly at higher energies, the order of the electronic states is often incorrectly predicted by *ab initio* procedures; furthermore, avoided and true crossing mean that the nature of the electronic state can change with bond length. Thus, careful monitoring of each electronic state in an *ab initio* calculation is imperative. The most obvious way is through monitoring the L_z expectation value; however, this cannot distinguish between two states of the same spin and symmetry (e.g. if the calculation has converged on the wrong state). We find a much more sensitive test for non-Σ and non-singlet states is the diagonal spin–orbit matrix element, which shows high stability across different quality wavefunctions. Furthermore, this can be directly compared to experiment as the matrix element is equal to $S\Lambda A$ where A is the standard experimental spin–orbit splitting constant. Diagonal dipole moments are another possible diagnostic, but generally only distinguishes between states of very different nature (e.g. different valency). The energy is somewhat useful, but must be considered with care; the errors in excitation energies can make this a misleading diagnostic, especially for low-level calculations. For example, CASSCF excitation energies may be double the true experimental excitation energies and higher electronic states, where incorrect state ordering even at relatively high levels of theory are common.

4.5. Potential energy curves

When considering *ab initio* PECs, we are most concerned with the parameters of each electronic state, particularly their energy relative to each other and to the ground state, the vibrational frequencies, equilibrium bond lengths and the long range behaviour. The choice of electronic structure theory procedure is limited by available methodologies in common quantum chemistry packages and time considerations. However, the most important limitation is the need for converged calculations and for continuous, smooth curves. These requirements are particularly difficult for the multi-reference methods that are required for stretched bonds and excited states. Furthermore, open-shell systems in general exhibit more complexity and difficulties with convergence.

Of course there are an infinite number of electronic states converging on any ionisation limit. This situation is not well treated by standard electronic stucture methods. However high-lying PECs have been successfully identified from negative energy scattering calculations (Sarpal *et al* 1991); under these circumstances the states are often best characterised via their quantum defects (Rabadán and Tennyson 1997). This procedure, unlike more standard basis set methods, becomes more accurate for very high-lying states as the error is often characterised by a constant shift in the quantum defect (Tennyson 1996, Schneider *et al* 2000). Quantum defect theory has been used to represent the spectrum of highly excited H_2 molecules with outstanding accuracy (Sprecher *et al* 2013, 2014).

The most ambitious use to date of scattering theory for excited bound states was by Little and Tennyson (2013), who considered Rydberg states of N_2 and mapped out in detail the many avoided crossings for this system. Use of this procedure would be interesting for transition-metal-containing molecules but would require further work to be done on improving the representation of the so-called target wavefunction (the wavefunction of the ionised system) used in the scattering model before really accurate results can be obtained for these systems.

Dissociation energies are calculated from two single-point energy calculations; therefore, very high level calculations are possible (Boyarkin *et al* 2013). However, there appears to be a relative lack of interest in this property and satisfaction with experimental results. This means that very high accuracy methodologies have not been extensively explored for transition metal diatomics.

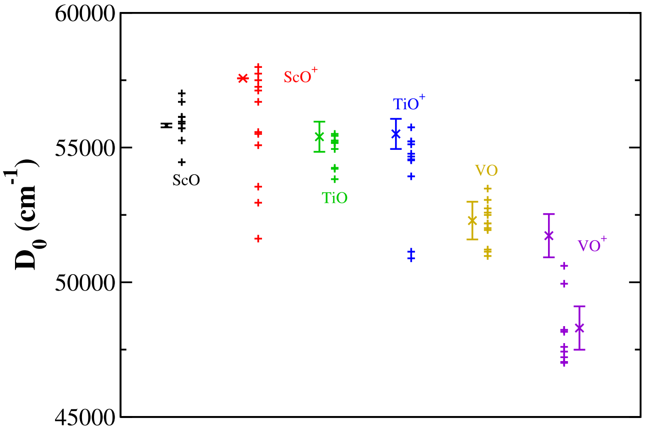

Figure 1. Calculated *ab initio* dissociation energies of neutral and charged transition metal oxides, using large basis sets and a variety of treatments of static and dynamic correlation compared to experiment (with error bars). *Ab initio* results are taken from Tilson and Harrison (1991), Bauschlicher and Maitre (1995), Nakao *et al* (2001), Miliordos and Mavridis (2007), and Miliordos and Mavridis (2010). Experimental results are taken from.Clemmer *et al* (1991), Loock *et al* (1998), Luc and Vetter (2001) and Jeung *et al* (2002).

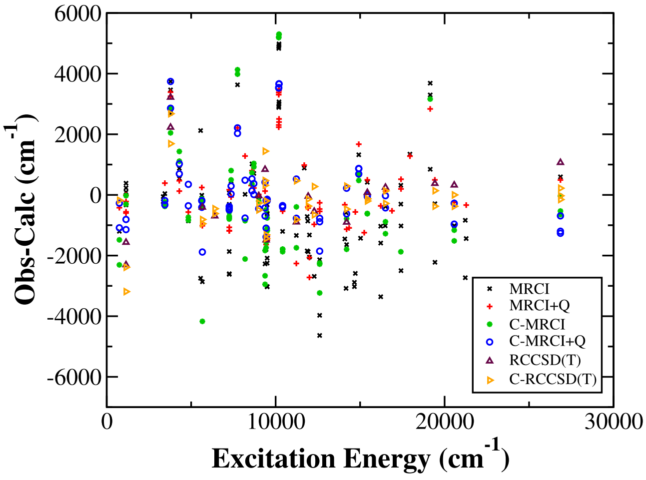

Figure 2. Observed minus calculated excitation energies of neutral and charged transition metal oxides, using large basis sets and a variety of treatments of static and dynamic correlation. *Ab initio* results taken from Jeung and Koutecky (1988), Langhoff (1997), Dobrodey (2001), Miliordos and Mavridis (2007, 2010), Hübner *et al* (2015) and McKemmish *et al* (2016a).

Figure 1 provides estimates of typical experimental and theoretical errors. This figure shows experimental dissociation energies (crosses) with error bars for early transition metal oxides, as well as theoretical predictions using a variety of high-level theoretical methods, specifically icMRCI, icMRCI +Q and R-CCSD(T) with and without semi-core correlation, all using cc-pVQZ basis sets. It is clear that the error in theoretical calculations and experiments are similar, around 500–2000 cm^{-1} from a total dissociation energy of 45 000–60 000 cm^{-1}.

Electronic excitation energies: Even for high quality calculations, the errors in the excitation energies for diatomic molecules often exceeds 1000 cm^{-1}, especially for the higher lying states, as shown in figure 2 for transition metal oxides. The very highest accuracy calculations even for the lowest electronic states is rarely more accurate than 100 cm^{-1}.

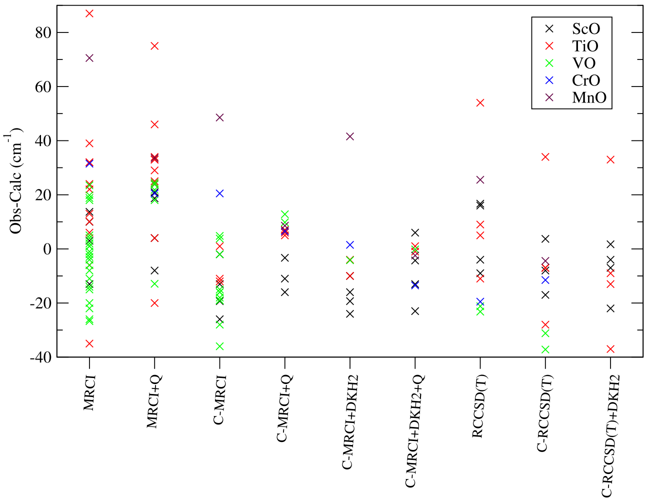

Figure 3. Observed minus calculated in the calculated vibrational frequencies of neutral transition metal oxides, using large basis sets and a variety of treatments of static and dynamic correlation. *Ab initio* results taken from Langhoff (1997), Miliordos and Mavridis (2007, 2010), Hübner *et al* (2015) and McKemmish *et al* (2016a).

Vibrational frequency: Typically, errors in vibrational frequencies are of order 10–30 cm^{-1}, as shown in figure 3. The error seems relatively independent of treatment of dynamic correlation, use of the Davidson correction (+Q), inclusion of core correlation and relativistic effects.

Rotational frequency: The equilibrium bond length for each vibronic state determines the rotational frequency of that state. Generally theory is able to reproduce experiment quite well. Errors of larger than 0.03 Å for high level calculations are rare, as shown in table 3. This table shows that the errors are normally significantly reduced by the inclusion of semi-core correlation (i.e. the 3s and 3p orbitals in the correlated space).

A 0.03 Å error in the bond length of a transition metal oxide will result in an error on order of 0.02 cm^{-1} for the rotational constant. This will only cause errors greater than 1 cm^{-1} for $J > 20$. A bond length error of 0.005 Å will not cause errors in excess of 1 cm^{-1} until approximately $J = 120$.

Couplings Diagonal spin–orbit coupling removes the degeneracy in energy between different spin components of non-singlet and non-Σ electronic states. For 3d transition metal diatomics, this is normally treated as a modification of the pre-existing PECs for an electronic state; it is generally of magnitude 10–250 cm^{-1}. Off-diagonal spin–orbit coupling gives intensity to spin-flipping transitions.

Ab initio spin–orbit matrix elements are surprisingly insensitive to the quality of the calculation. Lodi *et al* (2015) investigated the effects of different basis sets and treatment of dynamic electronic correlation against known experimental results and found that CASSCF/aug-cc-pVDZ was usually as reliable as the more expensive methodologies.

Electronic angular momentum matrix elements cannot generally be derived from experiment and must be calculated *ab initio*. Since there appear to be no benchmark results, we generally use high level theory, e.g. icMRCI/aug-cc-pVQZ. The bra and ket wavefunctions do not have to use the same set of CASSCF orbitals. Thus, we recommend optimising each separately (for a minimal number of states). Generally, we find these matrix elements to be of order 1.

Both the spin–orbit and electronic angular momentum matrix elements have a phase and sign (e.g. can be imaginary) depending on the phase of the component wavefunctions. These phases need to be treated carefully (Patrascu *et al* 2014, Yurchenko *et al* 2016b).

4.6. Dipole moments

While it is possible to improve PECs using experimental data, see next section, this is rarely possible and not generally recommended for DMCs (Lynas-Gray *et al* 1995).

Although the option of computing dipoles is standard in electronic structure programs, getting stable results for open shell systems is far from straightforward. Indeed the literature is full of examples of DMCs which show unphysical features, see Tennyson (2014). These features can arise from a variety of causes including (i) using inappropriate models such as Hartree–Fock or CC approaches which do not represent the dissociating wavefunction correctly and result in large, unphysical dipoles at large internuclear separations, see Barton *et al* (2013) for example; (ii) changes in orbital ordering: our preferred model for computing dipole moments is icMRCI; in this approach the orbitals are divided into frozen (fully occupied core orbitals), valence (used in the complete active and reference spaces) and virtuals (used in the CI step). Orbital swaps between these spaces at a particular geometry can result in sharp changes in dipole moments, see Lodi *et al* (2015) for example; (iii) even if the orbitals do not actually swap they can change character, for example from ionic to covalent, as a function of bond length with consequent changes in the dipoles. These changes in character may well be physical: most ionically bonded species dissociate to neutral fragments. However, orbital spaces which only contain orbitals with one of these characteristics can be or become unbalanced. In this context it should be noted that improved transition dipoles moments are obtained if different, optimal orbitals sets, so called bi-orthogonal orbitals, are used for the two states involved in the calculation (Schmidt and Bacskay 2007); (iv) symmetry contamination: as discussed above diatomic species contain significant symmetry properties, but most quantum chemistry codes do not use full ($C_{\infty v}$ or $D_{\infty h}$) linear molecule symmetry; an exception is the package Turbomole (Furche *et al* 2004), which however does not implement multireference methods and is therefore of limited interest to us.

Experience shows that care is needed to obtain smooth dipole moment and coupling curves. We have found that starting calculations using wavefunctions from a neighbouring geometry and starting calculations which use large basis sets with orbitals from calculations with smaller basis sets helps to maintain but does not guarantee smoothness.

Finally we note that measurements of transition absolute transition intensities for open shell systems are difficult and rare. An alternative is to measure the lifetime of the excited states. Such measurements have the significant advantage that

Table 3. The absolute error in the predicted equilibrium bond distance, Δr_e , for various electronic states of TiO and VO. The units of bond length are Å. For TiO, the source of *ab initio* data is Langhoff (1997), Dobrodey (2001) and Miliordos and Mavridis (2010). For VO, the source of *ab initio* data is Miliordos and Mavridis (2007), Hübner *et al* (2015) and McKemmish *et al* (2016a). All *ab initio* results included in the averaging are at least icMRCI or CCSD level, with basis sets of triple-zeta quality or better. CAS orbitals are optimised in different ways. The active space is (4s, 4p$_x$, 4p$_y$, 3d)/Ti, (4s, 3d)/V and (2p)/O or (2s, 2p)/O.

			No semi-core		With Semi-core	
Molecule	State	Config.	$\overline{\Delta r_e}$	max(Δr_e)	$\overline{\Delta r_e}$	max(Δr_e)
TiO	X $^3\Delta$	4s^{1}3d^1	0.014	0.017	0.002	0.003
	a $^1\Delta$	4s^{1}3d^1	0.014	0.018	0.004	0.005
	d $^1\Sigma^+$	4s^2	0.011	0.017	0.005	0.006
	E $^3\Pi$	4s^{1}3d^1	0.022	0.027	0.002	0.003
	A $^3\Phi$	4s^{1}3d^1	0.008	0.015	—	—
	b $^1\Pi$	4s^{1}3d^1	0.014	0.022	—	—
	B $^3\Pi$	3d^2	0.009	0.012	—	—
	C $^3\Delta$	4s^{1}3d^1	0.020	0.028	—	—
	c $^1\Phi$	3d^2	0.006	0.013	—	—
	f $^1\Delta$	4s^{1}3d^1	0.008	0.017	—	—
VO	X $^4\Sigma^-$	4s^{1}3d^2	0.005	0.004	0.003	0.002
	A′ $^4\Phi$	4s^{1}3d^2	0.004	0.004	0.004	0.003
	c $^2\Delta$	4s^{2}3d^1	0.008	0.015	0.004	0.015
	A $^4\Pi$	4s^{1}3d^2	0.001	0.001	0.004	0.003
	d $^2\Sigma^+$	4s^{1}3d^2	0.005	0.006	0.001	0.002
	B $^4\Pi$	3d^3	0.005	0.005	0.010	0.005
	e $^2\Phi$	4s^{1}3d^2	0.017	0.030	0.014	0.020

they do not require a knowledge of the population of states in the sample being studied. Lifetimes can be computed routinely from sets of Einstein A coefficients. This has been done recently for the line lists computed as part of the ExoMol project (Tennyson *et al* 2016a).

5. Nuclear motion calculation and improving the model

The above two sections describe the necessary ingredients for constructing a full *ab initio* spectroscopic model for open shell diatomic species. The resulting nuclear motion Schrödinger equations can then be solved. In the case of DUO (Yurchenko *et al* 2016b) this is done variationally by solving a $J = 0$ problem for each, uncoupled PEC and using these results to provide a basis set to solve the fully coupled, J-dependent problem. Solutions based on the direct integration of the coupled equations are also possible (Hutson 1994).

This direct method works well but is not without some issues. As the number of electronic states considerd grows, the number of coupling curves that needs to be considered grows as approximately the square of this number. The generation and handling of these curves can become quite cumbersome. However there are two further issues. First couplings may occur to states which are repulsive: this is actually the mechanism for the well-studied phenonomenon of pre-dissociation. Second, couplings to high-lying states which are not included in the model may also be important. Both of these situations are probably best dealt with by reverting to a pertubative treatment of the coupling via the use of effective constants.

Of course, as a model is extended to higher energies, the number of electronic states that might need to be considered grows rapidly. The issues here are not only the actual density of states but also the correct treatment of both so-called dark states, ones which do not have dipole-allowed transitions to the ground state, and the interaction of quasi-degenerate levels, often called resonances. Such resonances are well-known experimentally and often lead to intensity stealing by dark states which allows a few levels associated with these states to be observed. Attributing the correct vibrational (and sometimes even electronic) quantum numbers for the states is often difficult on the basis of observations alone. For molecules such as C_2 the *ab initio* theory is now accurate enough for electronic and vibrational states to be unambiguously identified (Bornhauser *et al* 2015); this is not true for systems containing transition metals (Yurchenko *et al* 2016b).

One way of improving on the ‘direct’, *ab initio* method for solving the spectroscopic problem is by addressing the corresponding inverse problem (Karkowski 2009, Weymuth and Reiher 2014), that is the task of determining the potential $V(R)$ which leads to a given set of energy levels E_{vJ}, typically obtained from experiment. One of the oldest ways to perform this task approximately is to use the semi-classical Rydberg–Klein–Rees method, see Karkowski (2009). A more precise strategy called inverse perturbation analysis based on perturbation theory has been suggested (Kosman and Hinze 1975, Weymuth and Reiher 2014) and a program implementing this approach was presented by Pashov *et al* (2000).

The gold-standard inverse problem usually involves determining a potential energy function, usually one represented in some pre-determined but flexible form, to a set of experimental-derived data such as energy levels or transition frequencies. The process involves minimising the standard deviation of observed minus calculated for these data. This methodology is increasing being used in problems involving coupled PECs, see Yukiya *et al* (2013), Walji *et al* (2015) and Patrascu *et al* (2014). A major advantage of performing such fits is that, at least with the BO approximation, one fit can be used to obtain spectra for all isotopologues. This means, for example, that a high accuracy fit to the (plentiful) data available for the main isotopologue can give excellent predicted spectra for isotopically substituted species. Of course one can also use data on several isotopologues simultaneously to determine corrections to the BO approximation; however, as shown by Watson (2004), one needs to be careful here as energy levels alone do not contain enough information to fully determine all the terms in this situation.

The usual problem in this approach is the lack of the experimental data. A standard situation is that the number of parameters required for adequate description of a PEC is greater than the number of vibrational states present in the experimental set, which makes the inverse problem underdetermined. In such situations the following approaches are commonly used: (i) approximating PECs with simpler model with smaller number of parameters; (ii) fixing some of the parameters to their *ab initio* values; (iii) constraining either the PEC or the expansion parameters to the *ab initio* values; (iv) 'morphing' the *ab initio* PEC using a simpler model (Patrascu *et al* 2014).

Another important issue is to decide on the fitting weights. The common practice is to set them inversely proportional to experimental uncertainty (Le Roy 1998). A very powerful alternative is the robust weighting procedure suggested by Watson (2003), where the weights are adjusted dynamically based on the quality of the experimental data.

For systems involving several electronic states using experimental data to determine the potential also brings the various coupling terms into play. These too can usually not be fully determined on the basis of energy levels alone. There is a further problem in that fitting can only involve a finite, usually small, number of states but the couplings link these to higher states not included in the fits. This issue can be resolved in a number of ways such as including pseudo-states to couple with or representing some of the associated splittings using effective Hamiltonian parameters. More work is probably required to fully understand how best to treat this issue.

6. Conclusion

In this topical review we address the issue of first principles theoretical treatment of diatomic molecules with special emphasis on the vibronic spectra of open shell species containing a transition metal atom. We advocate the direct solution of the nuclear motion Schrödinger equation; this methodology is sufficient to obtain quantitative answers. However, the current state-of-the-art in electronic structure methodologies is not. Indeed the predictions of what are considered high-level *ab initio* electronic structure calculations are so poor that even the correct ordering of the electronic states is hard to predict in many cases let alone the precise details required for spectroscopy.

Given this situation, experimental data will be required for the foreseeable future to help tune spectroscopic models for transition metal containing systems. In this context, the measurement of a large number of vibronic bands, rather than very high precision analysis of the rotational structure of a smaller number of bands is particularly useful. This can be best achieved in experimental conditions that lead to rotationally cold but vibrationally hot transitions. Similarly, there are rather few absolute intensity measurements for open-shell transition-metal-containing systems, however radiative lifetime measurements are equally useful for testing computed Einstein-A coefficients and appear to easier to perform. New lifetime measurements for a range of systems would be very helpful.

Finally, if anyone is still under the illusion that an *ab initio* description of transition-metal-containing diatomics is simple, we suggest that they look at the PECs of FeO as given in figure 1 of Sakellaris *et al* (2011). This system, which is of astrophysical importance, has 48 electronic states below 27 000 cm^{-1}, even before taking the splitting of levels into multiple terms by spin–orbit coupling into account!

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