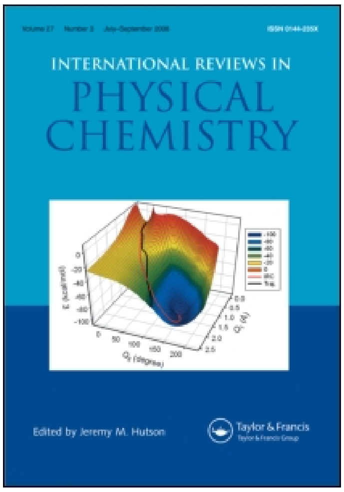

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Experimental benchmarks and phenomenology of interatomic forces: open-shell and electronic anisotropy effects

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Experimental benchmarks and phenomenology of interatomic forces: open-shell and electronic anisotropy effects

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This article gives a perspective view of some representative experimental information available on interatomic forces. They play a role in gaseous properties, but modern quantitative information comes from spectroscopy and molecular beam scattering. This latter technique is emphasized here: recent experimental results and consideration of physical properties of interacting species is complementary to progress of modelling based on *ab initio* or other quantum chemical calculations. Interactions involved in closed-shell–closed-shell species are considered to be typical of the so-called 'non-covalent' forces, although additional effects of a 'chemical' nature are demonstrated to be non-negligible in some cases. The partition of the interaction into van der Waals (repulsion + dispersion) and possibly electrostatic and/or induction components is analysed. Interactions involving open-shell species offer a most interesting phenomenology, because electronic anisotropy often provides further strength to the bonds, which are usually weaker than ordinary chemical bonds. Again, the focus is on experimental information (especially on scattering of magnetically analysed open-shell atoms) and on the understanding that comes from the analysis of the ample phenomenology accumulated. Additional terms such as those of specific 'covalent' nature appear in the partition of the interaction, besides those already mentioned. The extension of this approach for describing molecular anisotropies is also outlined.

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1. Introduction

1.1. *Motivation and dedication*

The interatomic and intermolecular interactions are crucial for understanding the structural and dynamical properties of matter. We review here advances from a phenomenological viewpoint. Theoretical progress (*ab initio*, semiempirical, perturbation theory) has also been impressive, but emphasis in this article is on experiments, especially on those achievements which come from molecular beam scattering techniques. Spectroscopy has also provided ample insights, especially because of modern coupling of sophisticated laser and molecular beam techniques. Regarding infrared laser spectroscopy applied to the study of weakly bound aggregates, Roger Miller, to whose memory this article is dedicated, presented an account [1] to the 2001 *Faraday Discussions* devoted to these issues. Regarding open-shell atoms (halogens) interacting with diatomic molecules, see Ref. [2] for a semiempirical approach and bound-state calculations, Ref. [3] for a quantum chemical study, and Ref. [4] for infrared laser spectroscopy in helium nanodroplets. This last field is reviewed in Ref. [5].

A consideration of what is experimentally established – both as quantitative information and as qualitative understanding – is also crucial for assessing the status of current quantum chemical efforts and possibly for providing a guide for their effective progress. A previous review in this journal [6] well summarizes the difficulties of *ab initio* molecular orbital theory associated specifically to drawbacks of the supermolecule strategy – the basis set superposition errors being often of the same order of magnitude of the quantities to be calculated. In view of their successes in various contexts, density functional theories (DFT) are intensively tailored and applied to fit the long-range intermolecular force problem; among the most recent ones, see Refs. [7–10]. Blending of *ab initio* and DFT approaches is of interest ([11] and references therein). Perturbation theories (such as the symmetry adapted version SAPT [12]), can also give information on the low-lying electronic states, of relevance for the open-shell interactions of interest to us (see for instance Ref. [13] and references therein). Other quantum chemical results will be quoted in the following when appropriate for the discussion of specific systems.

1.2. *Scope and outline of the paper*

This article has been written with the aim to show that molecular beam scattering has established benchmarks on range and strength of the interatomic interactions (both their isotropic and anisotropic components) and the resulting phenomenology is amenable to classifications and suggestive of correlation formulas with both descriptive and predictive capabilities. Section 2 sets the scene by establishing what is currently known on interactions of closed-shell species. This subject is typically referred to as that where a basic role is played by van der Waals forces, but additional 'chemical' contributions, such as those due to charge exchange, will be shown to be operative in some explicitly discussed circumstances. The main topic of this article comes in section 3, where open-shell effects are discussed. Many dynamical processes under focus of modern chemical physics are governed by interactions of open-shell species, beyond the atom–atom case. Typical examples include chemical reactions of excited halogen and oxygen atoms with H_2 molecule [14], photodetachment spectroscopy of weakly bound anions [15] and electronic to rotational energy transfer at ultracold temperatures [16]. However, the focus here will be mainly on atom–atom interactions. Progress on understanding atom–molecule and molecule–molecule interactions is briefly summarized in section 4. Final remarks and conclusions are in section 5. Experimental and theoretical tools are deferred to appendices A, B and C.

Appendix A gives an account of molecular beam scattering experiments – their basic configurations, and their information content for the characterization of intermolecular forces. Appendix B summarizes concepts and nomenclature for representation of the interatomic interaction and stresses its partition into different contributions, which can be correlated to the fundamental physical properties of the involved partners. The importance of anisotropies is a theme of this article, and a sketch of the theory for its extraction from molecular beam scattering experiments and for its adequate representation is given in appendix C. This allows us to define the nature of the interaction, to provide a unified framework for systems (or classes of systems) of apparently different characteristics, and to reliably anticipate the behaviour of systems not yet investigated, or very difficult to tackle.

This is essentially a review of case studies, with no aim at completeness. However, there are some items which have the flavour of novelty. Particular care is devoted to clearly define what has now been firmly established for the basic interaction currently referred to as 'van der Waals', which is present in all cases. In the approach of this article, where emphasis is placed on the characterization of the relative role of isotropic and anisotropic components of the total interaction, the van der Waals component is essentially associated with the former. The latter, typically originated by some extent of charge transfer as in the case of rare-gas halides or oxides, is often of the same magnitude order ($\sim$1 kJ mol^{-1}) as the van der Waals component. The present approach, which permits us to describe many systems within a unifying picture, can also be extended to more complex cases, such as those involving molecules.

2. Isotropic interactions and van der Waals forces

Phenomenological and correlation-formula approaches are often suggested by experimental observations and exploit some basic physical properties, with the aim of providing simple natural analytical forms for the interactions, which can also serve for predicting them in cases where experimental information is lacking or very difficult to obtain. This is particularly relevant for van der Waals forces, whose understanding is preliminary also for systems such as those where anisotropy effects occur, but where nonetheless the isotropic component is often dominant.

2.1. ^{2S+1}S atom–$^1S_0$ atom

In the process of understanding isotropic interactions one has to start with those systems where there is no additional contribution from anisotropies. These systems are those involving S atoms (electronic orbital angular momentum $L = 0$), and include also the case where one of the atom has spin **S**. We will deal with atoms in *LS* coupling in the next section.

Let us consider the interaction V of a $^1\mathrm{S}_0$ atom with another one, in a $^{2S+1}\mathrm{S}$ state. In the general representation (see equation (17) in appendix B) several terms often drop out and we are left with

$$V = V_{\mathrm{REP}} + V_{\mathrm{DISP}} \equiv V_{\mathrm{VDW}} \tag{1}$$

We identify the sum of these two terms with the so-called 'van der Waals' interaction, and this justifies the notation. We believe it important to adhere to this definition and to avoid (as often in the literature) inclusion of induction and electrostatic or (even worse) V_{CT} and V_{SS} terms, when referring to van der Waals forces, so that misleadingly they would be synonymous to intermolecular forces.

The decisive progress in understanding these systems started in the 1970s through molecular beam scattering (appendix A). Prototype systems are noble-gas–noble-gas interactions. As an example, figure 1 shows the integral cross-sections Q as a function of velocity v [17] and the differential cross-sections I as a function of the scattering angle θ [18]. The combined analysis permitted workers to discriminate between two potentials available in the mid-1980s [19, 20a] and which differ by only a few percent in the region of the well. For further references data on noble-gas–noble-gas interactions, see for instance Refs. [21] and [22] (the latter reports He–He striking oscillations due to the quantum mechanic effect of symmetry).

Other typical systems are H(^{2}S)–noble-gas. They had been studied in detail measuring $Q(v)$ in the 'glory' velocity range, where the high resolution of the experiment also

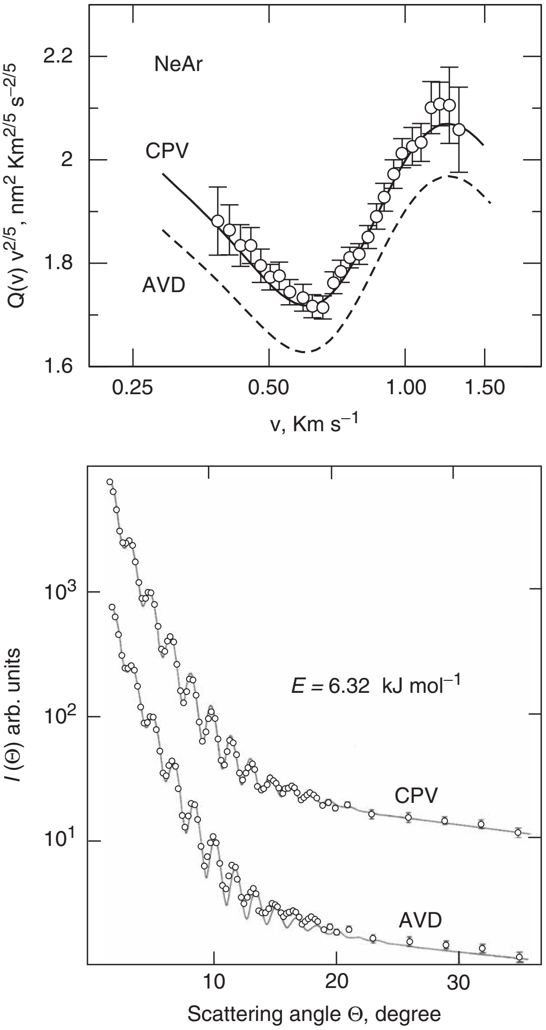

Figure 1. (Upper panel) Integral cross-sections Q for Ne–Ar collisions measured as a function of the Ne beam velocity v. Plotted cross-sections are multiplied by $v^{2/5}$ to make more evident the glory undulations. The solid line is the calculation performed using the CPV potential of Ref. [19], while the dashed line using the AVD potential of Ref. [20a]. The two potentials differ by 3.8% in the well depth, 2.9% in the equilibrium position and ~15% in the long-range attraction at interatomic distance of 5.5–6 Å. For more details see Ref. [17]. (Lower panel) Differential cross-sections I measured as a function of the scattering angle θ and at defined collision energy. Calculations (full lines) are performed using the CPV potential of Ref. [19] and the AVD potential of Ref. [20a]. For more details see Ref. [18].

permitted measurement of orbiting resonance effects [23]. Reviews of data on both noble-gas–noble-gas and atomic-hydrogen–noble-gas systems are available, such as [24, 25]. Other important systems which fall within the same category are alkali-metals(^{2}S)–noble-gas interactions [26–29], at least at the large distances of interest under cold and ultracold conditions. These classic studies are those of reference for accepted quantitative measurements of the involved interactions.

2.2. *Combination rules and correlation formulas*

Of the many proposals for ‘combination rules’, such as those allowing one to extract information on potential parameters for asymmetric systems, particularly the well depth ε and its position R_m, from the corresponding parameters of the symmetric (homonuclear) dimer, venerable ones are summarized in Ref. [30a]. More recent extensions are given in Refs. [31] and [32]. These rules generally are expected to hold for closed-shell–closed-shell systems. Interesting attempts to establish correlations between features of both atom–atom and atom–surface interaction potentials are described in Ref. [33].

In our group it has been found useful to represent the ε and R_m parameters by ‘correlation formulas’ in terms of the polarizabilities α_1 and α_2 of the interacting partners [34]. Specifically,

$$R_m = 1.767\frac{\alpha_1^{1/3} + \alpha_2^{1/3}}{(\alpha_1\alpha_2)^{0.095}} \tag{2}$$

where R_m is given in Å, α_1 and α_2 in Å^3 (1 Å = 0.1 nm),

$$\varepsilon = 0.72\frac{C_{\mathrm{LR}}}{R_m^6}, \tag{3}$$

where ε is given in meV (1 meV = 0.09648 kJ mol^{-1}) and C_{LR}, in meV Å^6, is an effective long-range London coefficient

$$C_{\mathrm{LR}} = 1.57.10^4\frac{\alpha_1\alpha_2}{(\alpha_1/N_1)^{1/2} + (\alpha_2/N_2)^{1/2}} \tag{4}$$

In equation (4), the units are as before (1 meV Å^6 = 9.648·10^{-8} kJ mol^{-1} m^6) and N_1 and N_2 are effective numbers of electrons which contribute to the polarizability of each atom.

Numerical coefficients in (2)–(4) were determined empirically [34]. The above equations effectively compact an extensive phenomenology accumulated over the years, as amply documented in Ref. [34], for a hundred atom–atom and atom–molecule systems (at least for small, nearly spherical, molecules).

In view of the emerging picture, also illustrated in appendix B, equation (2) reflects the fact that R_m depends on the balance between repulsion (represented by the sum of the ‘size’ contribution from the two partners as the cube root of their polarizabilities) and attraction (proportional to the product of polarizabilities).

Equation (3) exhibits interesting empirical evidence that for most systems the well depth ε is approximately 70% of the attraction in R_m, defined by the C_{LR} in equation (4).

Equation (4) is a generalization [34] of well-known formulas by Slater and Kirkwood [35] and by Pitzer [36]. The C_{LR} coefficient has to be considered as representing the effective attraction at intermediate and large interatomic distance R, including the contribution of the dispersion terms of higher order than R^{-6} [34].

The use of equation (4) for calculation of the global dispersion attraction in the region $R_m \leq R \leq 2R_m$ is exemplified in table 1, for two cases experimentally investigated. Its general validity permits us to estimate the long-range attraction in a great variety of systems, including also symmetric and asymmetric alkali dimers (see table 1 where

Table 1. Comparison of the long-range attraction $V(R)$, calculated at given distances R, from equation (4), with that reported in literature from experiments [21, 27] and from *ab initio* methods [37–39].

Systems	R (nm)	$V(R)$ (kJ mol^{-1}) Equation (4)	$V(R)$ (kJ mol^{-1}) Experiment
Ne–Kr	0.6	−0.0459	−0.0452 ± 0.004
	0.7	−0.0182	−0.0172 ± 0.001
Li–Xe	0.8	−0.1132	−0.1252 ± 0.006
	1.0	−0.0297	−0.0299 ± 0.001
		Equation (4)	*Ab initio*
Na–Na	1.0	−0.1147	−0.1130
	1.1	−0.0647	−0.0612
Rb–K	1.1	−0.1790	−0.1859
	1.2	−0.1061	−0.1050

Input data in equation (4): polarizability values, in Å^3, for Ne, Kr, Xe, Li, Na, K, Rb, are 0.4, 2.49, 4.04, 24.3, 23.6, 43.4 and 47.3, while effective electron numbers are 7.04, 11.46, 12.8, 1.22, 1.74, 1.85 and 1.92, respectively.

a comparison with *ab initio* calculations [37–39] is also reported), those of interest for collisions in cold and ultracold regimes.

The ε and R_m parameters can serve to build up a global representation of the potential, typically as a Lennard-Jones (12,6) function:

$$V(R) = \varepsilon\left[\left(\frac{R_m}{R}\right)^{12} - 2\left(\frac{R_m}{R}\right)^{6}\right] \tag{5}$$

The success of its extensive applications shows that this is a satisfactory description of potential wells, but repulsion is generally too steep and the long-range attraction tends to be overestimated by a factor as large as two [30a, 33a]. This motivated the search of more flexible multiparameter analytical forms [30b, 33b, 33c].

To overcome these drawbacks and still requiring a simple enough representation to be effectively implemented in molecular dynamics simulations, we offered a new model [40] motivated by previous analysis (Ref. [34] and appendix B), and designated $[n(x), m]$:

$$V(R) = \varepsilon\left[\left(\frac{m}{n(x)-m}\right)\left(\frac{1}{x}\right)^{n(x)} - \frac{n(x)}{n(x)-m}\left(\frac{1}{x}\right)^{m}\right] \tag{6}$$

where $x = R/R_m$ and $n(x) = \beta + 4x^2$. For the neutral–neutral case being considered in this section, $m = 6$. The additional parameter β has been found to vary in a limited range, from 8 to 10 going from 'soft' (highly polarizable) to 'rigid' (small polarizability) systems.

The usefulness of equation (6) is illustrated in figure 2, where the Ar–Ar system is analysed and the interaction potential from equation (6) is compared with that from equation (5) and with the experimental one proposed by Aziz [20b]. As can be appreciated from the upper panel of the figure, where a blow up of the long-range region is shown, the $[n(x), m]$ and Aziz potentials agree within a few percent while

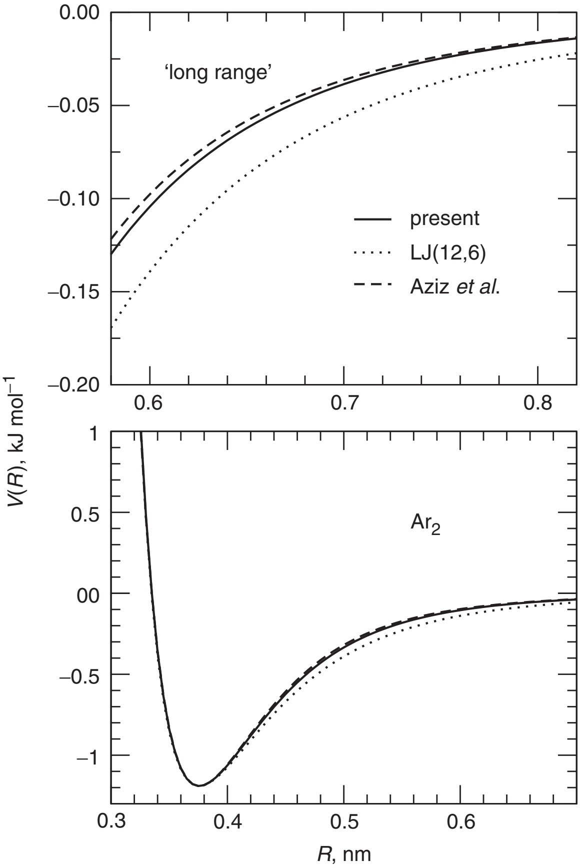

Figure 2. The Ar_2 interaction potential $V(R)$ obtained by Aziz (dashed line) [20b] compared with those parameterized as LJ(12,6) (equation 5, dotted line) and $[n(x), 6]$ (equation 6, full line) by using the same ε and R_m of Ref. [20b].

LJ(12,6) greatly overestimates the attraction. In the repulsive region, the $[n(x), m]$ potential model is much less steep than LJ(12,6) and gets closer to the Aziz potential. A calculation of the scattering integral cross-sections, in the thermal collisional energy range, leads to a nearly identical result for the $[n(x), m]$ and Aziz potentials while for the LJ(12,6) potential a velocity shift of 5% of the glory pattern and of 16% of the absolute value of the cross-sections is observed. Reference [40] and the next section show that the $[n(x), m]$ model can be easily extended to ionic systems.

2.3. ^{2S+1}S ion–$^{1}S_0$ atom

Here, exemplary case studies are those where the ion is an alkali (M^+) or a halogen (X^-) and the atom is a noble gas. Then

$$V = V_{\mathrm{REP}} + V_{\mathrm{DISP}} + V_{\mathrm{IND}} = V_{\mathrm{VDW}} + V_{\mathrm{IND}} \tag{7}$$

Correlation formulas (2) and (3) have been generalized [41] to cover this case, using a parameter ρ, representative of the relative role of V_{DISP} with respect to V_{IND} in the neighbourhood of R_m. If the ion has charge q and polarizability α_i, and the atom has polarizability α_a,

$$\rho = \frac{\alpha_i}{q^2[1+(2\alpha_i/\alpha_a)^{1/2}]\alpha_a^{1/2}} \tag{8}$$

$$R_m = 1.767\frac{\alpha_i^{1/3}+\alpha_a^{1/3}}{[\alpha_i\alpha_a(1+(1/\rho))]^{0.095}}, \tag{9}$$

where R_m is in Å if α's are expressed in Å^3. Again, ε is 72% of the attraction in R_m. The working formula is

$$\varepsilon = \frac{5.10\times10^3}{R_m^4}q^2\alpha(1+\rho), \tag{10}$$

where α is in Å^3 and ε is in meV. Equations (8)–(10) describe an ample phenomenology as documented in Ref. [41]. Examples ($\mathrm{Cl^-}$–Ar, $\mathrm{Cl^-}$–Kr and $\mathrm{Ca^{++}}$–He) are reported in table 2, while further extensions to $\mathrm{M^+}(^1\mathrm{S}_0)$ and $\mathrm{X^-}(^1\mathrm{S}_0)$ interactions are to be found in Ref. [47]. The ε and R_m parameters can be also inserted in equation (6), where $m=4$ for ion–neutral and $m=1$ for ion–ion systems (see Ref. [40]) to generate the $V(R)$ potential function. Evaluation of ρ can be hard, especially for ion–molecule cases.

For a generalization of the approach it is expedient to explicitly consider the ion–neutral interaction as a sum of V_{VDW} and V_{IND} (see equation 7). The first term is to be estimated by the same ingredients (polarizabilities as in the previous section) and possibly parameterized as in equation (6), again with $m=6$, the additional term (expressing the charge-induced-dipole interaction) being parameterized as in appendix B. Two typical examples are reported in figure 3, where the role of the interaction component is also illustrated.

So far, we discussed cases where V reduces either to V_{VDW} or to $V_{\mathrm{VDW}}+V_{\mathrm{IND}}$. Further analysis shows that there are situations where the above, limiting schemes need

Table 2. Features of the interaction potential for closed-shell ion–rare-gas atom systems. The depth of the potential (ε) is in kJ mol^{-1} and the equilibrium distance (R_m) is in nm.

	$\mathrm{Cl^-}$–Ar		$\mathrm{Cl^-}$–Kr		$\mathrm{Ca^{2+}}$–He	
Systems	ε	R_m	ε	R_m	ε	R_m
Predicted values	7.3	0.377	10.1	0.385	13.5	0.235
Experimental [42]	6.3	0.371	9.3	0.383	–	–
Ab initio [43]	6.0	0.369	8.6	0.372	14.5*	0.236*
Semiempirical [44]	6.2	0.375	–	–	–	–
Universal scaling law [45]	9.6	0.331	10.3	0.355	–	–

*Ref. [46].

Input data in equations (9), (10): polarizability values, in Å^3, for He, Ar, Kr, $\mathrm{Cl^-}$ and $\mathrm{Ca^{++}}$ are 0.2, 1.64, 2.49, 3.82 and 0.52, while ρ values for $\mathrm{Cl^-}$–Ar, $\mathrm{Cl^-}$–Kr and $\mathrm{Ca^{++}}$–He are 0.787, 0.778 and 0.073, respectively.

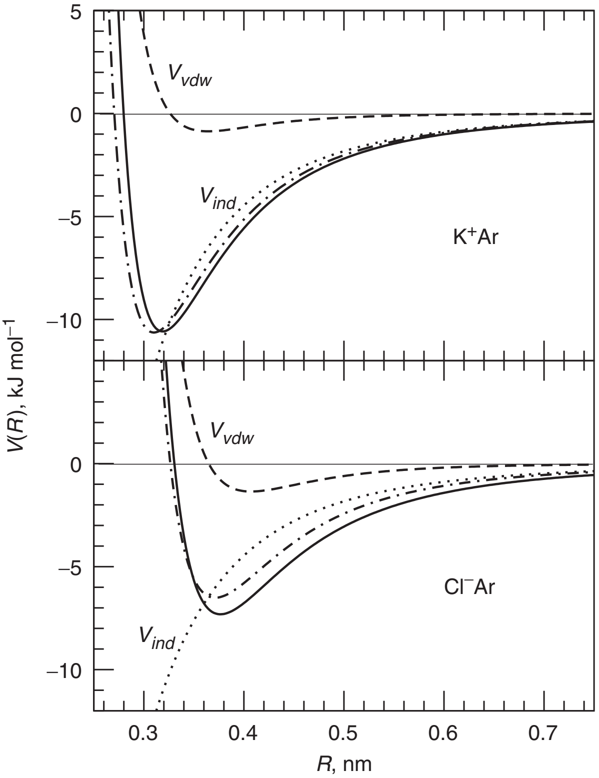

Figure 3. Full lines are calculated according to equation (6), where $m = 4$. The potential parameters ε ($\varepsilon = 10.6$ and $7.33\,\mathrm{kJ\,mol^{-1}}$, for K^+–Ar and Cl^-–Ar systems, respectively) and R_m ($R_m = 0.319$ and 0.377 nm for K^+–Ar and Cl^-–Ar systems, respectively), have been obtained by using correlation formulas in equations (8)–(10). Dashed lines describe the V_{VDW} components, parameterized according to equations (2)–(4) and (6), while dotted lines represent V_{IND} defined as in the appendix B. The calculations demonstrate that in the neighbourhood of the potential well, $V_{\mathrm{DISP}}/V_{\mathrm{IND}}$ ratio is about 0.30 and 0.75, while the ratio between well depths, associated to V_{VDW} and V, is about 0.1 and 0.2, for K^+–Ar and Cl^-–Ar systems, respectively. The potential parameters have been estimated by using using $\alpha_{K^+} = 0.85\,\text{Å}^3$, $a_{Cl^-} = 3.82\,\text{Å}^3$ and $\alpha_{Kr} = 2.49\,\text{Å}^3$.

some close attention, which brings additional insights for the comprehension of the nature of these interactions. These are some examples:

(i) *$^1S_0$ atom–$^1S_0$ atom, both highly polarizable.* Atoms of the IIB group have low HOMO-LUMO gap and thus high α. An application of correlation formulas and a proper scrutiny of small deviations between predictions and experimentally determined values [48a] allow the quantifying of the possible ‘chemical’ contribution, nearly absent for Zn–Zn, sizeable for Hg–Hg, and intermediate for Cd–Cd (see table 3).

These systems indicated that weak covalent (or ‘chemical’) contributions to the bond increase along the series of group IIB atoms. In retrospect, similar effects had been anticipated, e.g. in Ref. [48b] for a study of the Li–Hg system.

(ii) *Stiff $^1S_0$ atom–soft $^1S_0$ atom.* The example is metastable helium He*($^1S_0$), with Ar [49, 50]. The He* can be imagined as a He^+ core and an extended electron

Table 3. Interaction potential features of Group IIB atoms. The depth of the potential (ε) is in kJ mol^{-1} and the equilibrium distance (R_m) is in nm.

	Equations (1)–(3)		Exp. [48]	
Systems	ε	R_m	ε	R_m
Zn–Zn	2.74	0.468	3.34	0.462
Cd–Cd	2.57	0.457	3.95	0.433
Hg–Hg	2.40	0.446	4.54	0.366

Input data in equations (1)–(3): polarizability values, in Å^3, for Zn, Cd and Hg are 7.1, 6.0 and 5.1, while effective electron numbers are 7.78, 8.55 and 9.10, respectively.

orbiting far away. So the interaction is the expected van der Waals term at large distance. At intermediate and short range an appreciable induction term sets in especially when the argon atom get closer to the ionic core He$^+$ than the orbit of the excited electron of helium. In such conditions the whole diatom tends to be in a Rydberg state, with the He$^+$ core inducing a dipole on the charge distribution of argon.

(iii) *Small* $^1S_0$ *ion–highly polarizable* ^2S *atom*. This case includes the symmetric (MM)$^+$ dimers in [51], where M are alkali metals. Terms of induction and charge-transfer type acquire importance, accounting for the increase stability of these dimer ions with respect to the corresponding neutral dimer M$_2$ [51].

(iv) ^2S *ion–*$^1S_0$ *atom, with* A_A *comparable to or coincident with* I_D. As for (iii), where the electron affinity (A_{A}) of the electron acceptor is comparable to and coincident with the ionization potential (I_{D}) of the electron donor (see appendix B), a charge-transfer ('chemical') contribution can be of relevance, and

$$V = V_{\mathrm{REP}} + V_{\mathrm{DISP}} + V_{\mathrm{IND}} + V_{\mathrm{CT}} \tag{11}$$

The He$^+$–He system can be considered as prototypical and a well-studied example is the He$^+$–Ne system [52]. V_{CT} substantially affects both the binding energy and the sequence of molecular states for these two cases.

These last examples are forerunners of the quite peculiar and decisive role that charge transfer will be seen to play in the general open-shell–closed-shell interaction systems, to be discussed in the following section.

3. Anisotropic interactions and open-shell effects

3.1. *General*

The basic contributions to V (see appendix B) show features associated to the electronic anisotropy, and therefore a dependence of the orientation of the (non s) external orbitals. For a quantitative description, one must take into account the coupling schemes for the electronic orbital (**L**) and spin (**S**) angular momenta and therefore of the magnitude of the resulting angular momenta and of their projections in the interatomic potential field.

In appendix C a summary is given of the coupling schemes used for the representation of the global potential energy of the system, including possibly the spin–orbit relativistic coupling, to take into account fine structure effects. The viewpoint is motivated from a collisional approach to the atom–atom interaction, which is adopted in the interpretation of the scattering experiments. See also Ref. [53]. In this article, we will be mainly concerned with establishing how the basic contributions to V may vary their relative role as we move from one system (or a class of systems) to another.

Our analysis, which involves a selection of case studies, will appear to be sufficiently ample although not easily amenable to simple basic facts. Those systems which we discuss have some prototypical character and their understanding will possibly be of help in anticipating features for those for which experimental information is incomplete or lacking.

3.2. ^{2S+1}P *atom*–$^{1}S_0$ *atom*

The main features of anisotropic atom–atom interactions emerge when one of them is in a P state and the other one has a closed shell (typically, a noble gas). Two limiting cases bracket the phenomenology according to the open-shell characteristics of the P atom.

(i) *Highly polarizable P atoms (low A_A)*. Several atoms of the periodic table show a low electron affinity. Prototypes here are excited first or second group metals, alkalis (^{2}P) or mercury (^{3}P) being the more common examples since the early days of photochemistry, due to the favourable spectroscopic features of their resonance lines.

The excited electron is in a p atomic orbital, much more diffuse than the ionic core. While there, the electron determines a high polarizability and a strong anisotropy in the external electronic charge distribution of the atom. The polarizability is itself strongly anisotropic and there is a pronounced permanent quadrupole moment. For example, in the case of a p^1 configuration, the quadrupole moment is proportional to $\langle r^2 \rangle$, the average of the square of the radial distribution of the p orbital [54].

For these systems, we represent V as in equation (7), where all the components vary both with R and *with the orientation of the p orbital*, i.e. with the projection Λ of $\mathbf{L}$ into $\mathbf{R}$ (as sketched in appendix C). For a P state ($L = 1$), we can thus label the interaction as V_Σ or V_Π, according to whether $\Lambda = 0$ or $\Lambda = 1$, as customary in spectroscopy; alternatively, as appropriate in molecular beam scattering, as V_0 and V_2 (see again appendix C) and thus as an isotropic and an anisotropic component. Both experimental and theoretical information on the interaction in ^{2}P-alkali-metal–^{1}S$_0$-noble-gas systems are available. Some are in Ref. [55], while those on second-group metal atoms (^{3}P, essentially IIB group) with noble-gas are in Ref. [56].

(ii) *P atoms with high A_A*. Relevant experiments (molecular beam scattering without [57] and with [58] magnetic selection and spectroscopy [59]) involve doublets (halogen atoms F(^{2}P), Cl(^{2}P), Br(^{2}P), I(^{2}P)) and triplets (O(^{3}P), S(^{3}P)). Figure 4 reports experimental data on the KrCl systems obtained by scattering magnetically selected Cl atoms onto Kr targets. The experimental data demonstrate the effect of the different Cl atom polarization on the scattering,

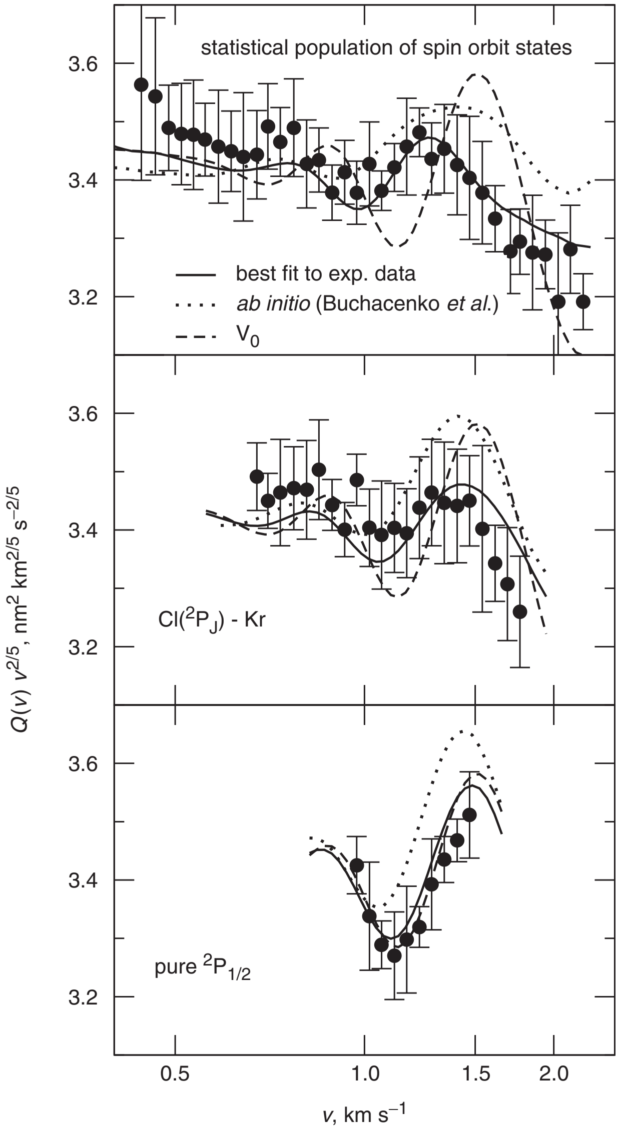

Figure 4. Integral cross-section $Q(v)$ for scattering of a Cl (^2P_j) atom beam by Kr, as a function of the beam velocity v, measured at different population of the chlorine atom in $^2P_{1/2}$ state, increasing from top to bottom. The dashed line, calculated by using the spherical component V_0, is reported to show the effect of the interaction anisotropy. The dotted lines are calculation using *ab initio* interaction potentials [61b].

which relates to the interaction anisotropy. Informative theoretical calculations and discussions are of interest [60, 61].

The picture and formalism are similar to the previous case, if one figures out the underlying physics as due to an electron hole of *p*-symmetry, rather than to an electron in a *p* orbital. Although F, Cl, O and S atoms show rather compact p^5 and p^4 configurations corresponding to a small anisotropy of the charge distribution (values of the polarizability anisotropy are reported in Ref. [62]), the analysis of the interaction deserves close attention. The terms describing the interaction are essentially the same as in the previous case, equation (7), only when V_{CT} is negligible. Both experiments [57, 58] and theoretical calculations [60, 61] suggest that this is the case for systems involving He or Ne (high ionization potential, I_{D}). In particular, scattering experiments provide accurate isotropic components, V_0, of the open-shell–closed-shell interactions (He, Ne).

3.3 *Charge transfer and bond stabilization*

When ‘targets’ are the heavier rare gases – those with lower I_{D}, such as Kr or Xe – then electron anisotropy becomes appreciable, and will be correlated to an additional, non-negligible contribution of a charge-transfer term, V_{CT}, to the total interaction V. The effect varies selectively with the symmetry of the molecular orbital that is formed, because strictly related to the charge-transfer mechanism. Specifically, it depends on the amount of overlap between the atomic orbital which tends to yield the electron and the one which is offering to accept it. The effect is small in V_0, crucial in V_2. Its understanding is a challenge, both experimentally and theoretically, because the observed phenomenology is rather complicated.

In Refs. [63] and [64], we have tried to disentangle the riddle by:

- *Introducing* the concept of ‘bond stabilization by charge transfer’ V_{CT}

$$V_{\mathrm{CT}} = \frac{H_{\mathrm{AD}}^2}{\Delta E} \tag{12}$$

(see appendix B, and note that V_{CT} and H_{AD} were denoted V_{X} and β in Ref. [63]).

- *Discussing* the nature of the isotropic and anisotropic terms, V_0 and V_2, which appear (appendix C) in the picture that we have chosen for the total interaction:

$$V_0 \cong \bar{V}_{\mathrm{INT}} \cong \bar{V}_{\mathrm{REP}} + \bar{V}_{\mathrm{DISP}} = \bar{V}_{\mathrm{VDW}} \tag{13}$$

(the bar indicate averaging over relative orientations)

$$V_2 = \pm\frac{5}{2} V_{\mathrm{CT}} = \pm\frac{5}{2}\frac{H_{\mathrm{AD}}^2}{\Delta E}. \tag{14}$$

The sign ±, being dependent on the symmetry of the electronic ground state of the system, is plus for oxides and sulfides (Π state) and minus for halides (Σ state). Some potential features of F(^{2}P) and Cl(^{2}P) rare-gas systems are summarized in tables 4 and 5. Reported data demonstrate that V_0 is basically V_{VDW} and emphasized the effect of V_{CT} in stabilizing the ground state of heavier rare-gas fluorides and chlorides.

- *Defining* the value of the H_{AD} term, on a absolute scale, at a given value of interatomic distance, $R = \sigma$, where $V_0(\sigma) = 0$, i.e. where attraction and

Table 4. Potential well depth ε (kJ mol^{-1}) and equilibrium distance R_m (nm), for V_0 and V_Σ interactions in F–Rg systems, as obtained from the analysis of scattering experiments. In parenthesis, potential parameters are also reported, referred to the V_{VDW} interaction component, estimated from equations (2)–(4) using an average polarizability value of F ($\alpha = 0.56\,\text{Å}^3$).

		F–He	F–Ne	F–Ar	F–Kr	F–Xe
V_Σ	ε	0.222	0.733	1.158	4.564	15.61
	R_m	0.300	0.290	0.312	0.283	0.231
V_0	ε^{a}	0.203 (0.238)	0.405 (0.437)	0.656 (0.653)	0.695 (0.733)	0.781 (0.750)
	$R_m{}^{a}$	0.303 (0.307)	0.315 (0.318)	0.350 (0.357)	0.365 (0.373)	0.378 (0.395)

[a] Quoted values are close to those of Ne ($\alpha = 0.40\,\text{Å}^3$) – Rg interactions as discussed in Ref. [34].

Table 5. Potential well depth ε (kJ mol^{-1}) and equilibrium distance R_m (nm), for V_0 and V_Σ interactions in Cl–Rg systems, as obtained from the analysis of scattering experiments. In parenthesis, potential parameters are also reported, referred to the V_{VDW} interaction component, estimated from equations (2)–(4) using an average polarizability value of Cl ($\alpha = 2.18\,\text{Å}^3$).

		Cl–He	Cl–Ne	Cl–Ar	Cl–Kr	Cl–Xe
V_Σ	ε	0.301	0.736	1.692	2.868	6.153
	R_m	0.339	0.338	0.368	0.358	0.317
V_0	ε^{a}	0.256 (0.258)	0.473 (0.532)	1.240 (1.185)	1.606 (1.470)	1.948 (1.714)
	$R_m{}^{a}$	0.349 (0.360)	0.361 (0.364)	0.388 (0.388)	0.395 (0.399)	0.406 (0.415)

[a] Quoted values are close to those of Kr ($\alpha = 2.49\,\text{Å}^3$) – Rg interactions as discussed in Refs. [34] and [58g].

repulsion balance and scattering experiments [57, 58] are most sensitive to the anisotropy V_2 (this corresponds to defining the parameter C in appendix B).

Available information has been compacted empirically [63, 64] by the formula

$$H_{\mathrm{AD}}(\sigma) = 39.3\sqrt{\varepsilon}, \tag{15}$$

where ε is the well depth of V_0 in kJ mol^{-1}.

- *Allowing* the quantification of the role of V_2, and therefore V_{CT}, according to the nature and sequential characteristics of the molecular states of the system. Figure 5 considers the specific case of Cl–Xe system and illustrates the emerging picture.

The specific case presented in the figure is paradigmatic: in general, Σ states are those mostly affected by charge transfer, while Π states much less so [108]. This is due to the different value of the overlap integral $\mathcal{S}$, between atomic orbitals exchanging the electron ($\mathcal{S}_\Pi \ll \mathcal{S}_\Sigma$ [65]). Thus the isotropic term V_0, which is mainly influenced by Π states, is little affected by charge transfer, as illustrated also by data in tables 4 and 5. Appendix C shows how to combine V_0, V_2 and spin–orbit splitting to define effective 'adiabatic' potentials that govern the collisions. The analysis demonstrates that spin–orbit coupling tends to hinder, for certain symmetries, the alignment of orbitals that is the prime cause of the V_{CT}: this happens whenever $|V_2| < \Delta$, the spin–orbit splitting, and the collision complex is best seen as a 'diatom' rather than a (weakly bound) molecule.

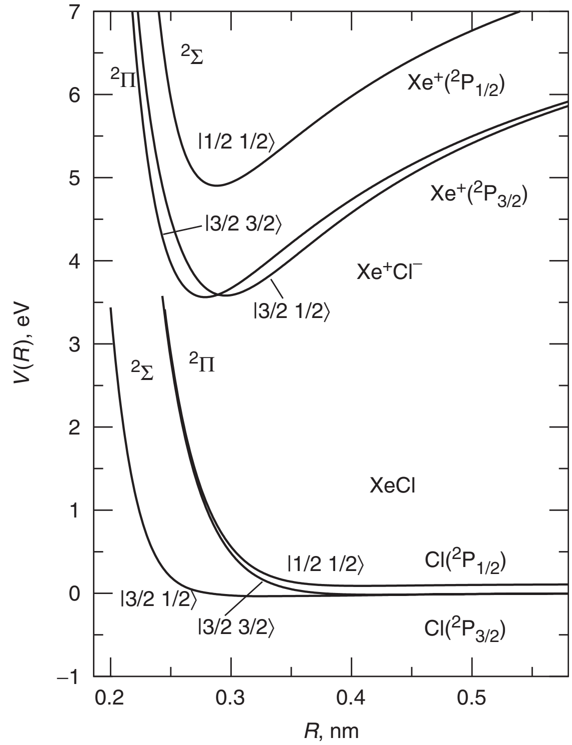

Figure 5. Manifold of interaction potential curves asymptotically correlating with Cl (^2P_j)–Xe and Cl^-–Xe^+ (^2P_j) atomic states (1 eV = 96.48 kJ mol^{-1}). The leading components of V are V_{VDW} and V_{CT} in the low lying neutral states and V_{VDW}, V_{IND}, V_{CT} and V_{ELECTR} in the ionic excited states. For more details, see Ref. [63]. At intermediate interatomic distances the states are labeled as $|J\Omega\rangle$ (see appendix C).

For the S(^3P)–noble-gas systems, both scattering experiments and *ab initio* calculations are available [61]. Their combination confirms the picture here illustrated for systems including halogen (^2P) atoms.

3.4. *^{2S+1}P ion –$^1S_0$ atom*

In most known examples involving P-state ions the situation fits in the framework outlined above, when proper account is given of the relative importance of some of the terms contributing to V. Figure 6 provides an example.

It has to be noted that the above framework encompasses the situation that occurs whenever A_A is considerably smaller than I_D. If A_A and I_D become comparable, the effect of V_{CT} cannot be treated as a perturbation, but tends to become 'resonant' (appendix B).

The comparative analysis of systems in both the perturbative and in the resonant regime [63, 64] has allowed us to follow the passage from typically van der Waals interactions to a one-electron chemical bond. Prototypes are systems involving an open-shell atom and He or Ne from one side, and H_2^+ and the noble-gas dimer ions Rg_2^+,

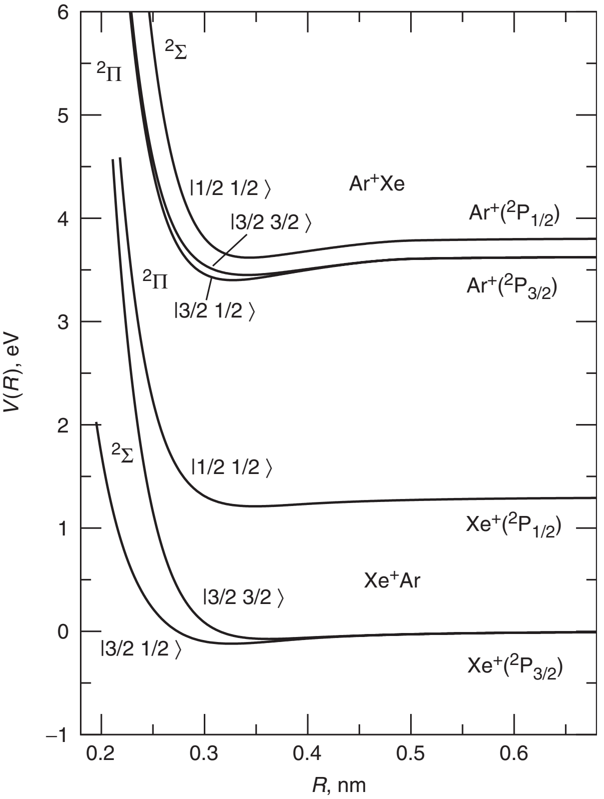

Figure 6. Manifold of interaction potential curves asymptotically correlating with $Xe^+(^2P_j)$–Ar and $Ar^+(^2P_j)$ –Xe atomic states ($1\,eV = 96.48\,kJ\,mol^{-1}$). The leading components of V are V_{VDW}, V_{CT} and V_{IND} for all states. For more details, see Ref. [63]. See also figure 5.

from the other. A variety of phenomena of apparently different nature has been compacted and described within a unifying picture [63, 64] by taking into account the role of the various components of V_{INT}, particularly V_{CT}. They include also harpooning and ion recombination processes.

3.5 *Dications*

The identification of the nature of the various components contributing to V and their proper description in terms of the physical properties of the involved species serve to understand features of apparently more complicated systems. Interesting examples are provided by diatomic dications, for which we discuss two cases:

(i) He_2^{+2}. This was the object of a pioneer study by Pauling [66]. The system is metastable in the ground $^1\Sigma$ state, where – in the spirit of our phenomenological approach – we write

$$V = V_{REP} + V_{ELECTR} + V_{COV} \tag{16}$$

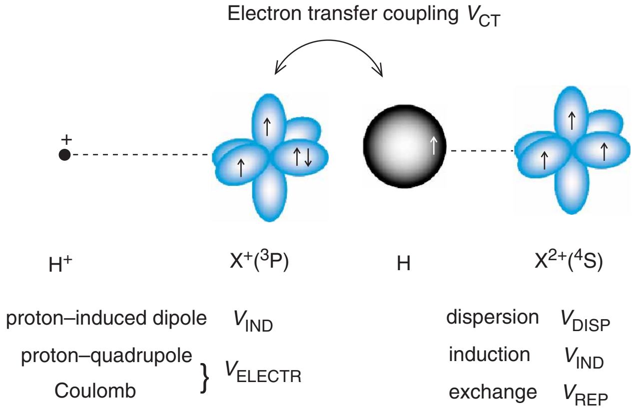

Figure 7. Atomic orbitals, exchanging the electron in HX^{+2} systems. The role of the leading interaction components is also indicated.

It is the term V_{COV} (see appendix B), including chemical contributions which arise here from the overlap of the ^1s orbitals, that contrasts the strong repulsion in V_{ELECTR}, originating from the Coulombic He^+–He^+ interaction.

(ii) HX^{+2} (X = F, Cl, Br and I). The states of these dications correlate dissociatively with atomic states such as X^{+2} (^4S, ^2D)–H (^2S) and X^+ (^3P, ^1D, ^1S, . . .)–H^+. Basic ingredients to describe the interaction are those that have been under focus in this article. Specifically, the H_{AD} parameter that fixes the V_{CT} interaction term, has to be estimated for any symmetry of the involved atomic orbitals and from their overlap (see figure 7 and appendix B). Figure 8 shows the case of HBr^{+2} and more details on the lower molecular states of the HX^{+2} systems are presented in Refs. [67–69]. The potential curves have been built up considering V as combination of terms illustrated in figure 7 and modelled according to the prescriptions presented in this paper. The results are in good agreement with *ab initio* calculations, and the representation of V in terms of physically motivated interaction components allows understanding of how the metastability degree of HX^{2+} varies along the series, being correlated to the role of the V_{CT} contribution. It also allows an accurate estimate of quantum levels, life-times, Franck–Condon factors and Coulombic explosion probabilities [67–69].

4. Final remarks

4.1. *Towards atom–molecule and molecule–molecule interactions*

Among the simple systems that have been under investigation in our group combining experimental information, phenomenological appraisal and representation of the involved interactions, we list atom–molecule [70–73], ion–molecule [74] and molecule–molecule [75, 76] case studies. The latter are on dimers of the major components of atmosphere, N_2 and O_2, and the interactions among them.

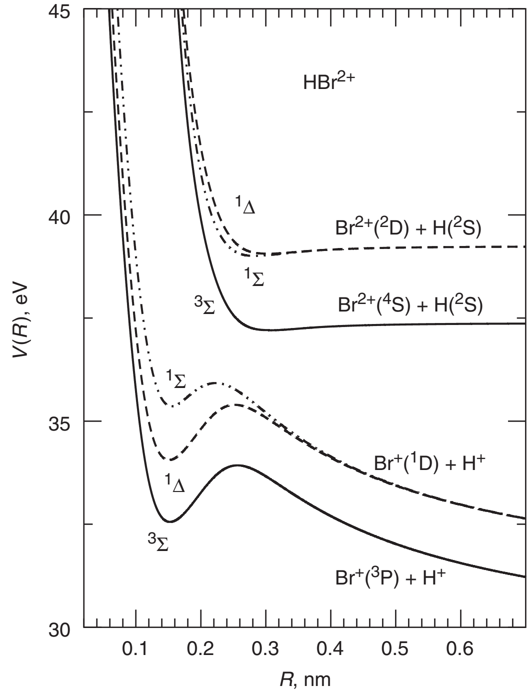

Figure 8. Potential energy curves for the various molecular states of the HBr^{+2} dication (1 eV = 96.48 kJ mol^{-1}). They have been obtained with the procedure described in detail in Refs. [67–69]. Only the states coupled by the electron exchange are reported.

The characterization of these and other systems has been and will continue to be of great help to widen our understanding of intermolecular forces and to assess their effects on molecular dynamics of elastic, inelastic and reactive processes. Further progress can be achieved by the planning of new experiments on sample systems, as well as from accompanying quantum chemical calculations. What appears to be crucial is the systematic classification of the main contributions to the interaction in terms of the basic physical properties of the involved species, in order to assess the established behaviour of investigated systems and to predict their effects on unknown systems of ever increasing complexity. For these, at sufficiently long-range, the components that contribute to V can be assumed to be the same as for the atom–atom cases of principal concern in this article. Account of molecular anisotropy is of course to be properly made, and it is of prime importance to stress that in the molecular case the nature itself of the various terms may be extremely specific. Also, a word of caution has to be said of inherent limits of pairwise atom–atom additive based interaction potentials of widespread and almost universal use in molecular dynamics simulations.

Here a specific set of features, regarding extensions to the case of interactions involving molecules, will be emphasized:

- V_{CT} depends again on the overlap between orbitals exchanging the electron. It exponentially decreases with R and selectively varies with the relative orientation and symmetry of orbitals involved in the exchange.

- V_{ELECTR} relates to the charge distribution on the molecular frame, obtainable, in principle from *ad hoc ab initio* or other calculations.
- V_{IND} arises from the interactions between induced multipoles on a species and the permanent charge distribution on the other. In general it depends on the product of the polarizability of the first species and the square of the resulting electric field due to the charge distribution on the other. Therefore it follows a non-additive behaviour [77, 78].
- V_{VDW} results from the balancing of size repulsion (short-range) with dispersion attraction (long-range). This is the interaction component more difficult to evaluate, but this article indicates a route to proceed towards its modelling.

4.2. *Prospects for future work*

Further general indications follow with the aim of pointing out both what can be considered as well established, and towards which directions we are focusing our efforts. The basic molecular quantity to describe both V_{VDW} and V_{IND} is the polarizability. Its accurate evaluation can be often elusive. In the molecular case, it is a tensor, which can be defined and decomposed in terms of tensorial components, such as those associated to the bonds and to the lone pairs [79–81]. The definition and valuation of these components is mandatory for the accurate estimate of V_{VDW} and V_{IND} [82]. For small and homonuclear diatomic molecules (H_2, N_2), the outer electronic charge distribution can be approximately represented as an ellipsoid, whose dimensions are related to the polarizability tensor components [82]. In this case the molecule can be modelled as having a single dispersion-induction centre.

Small heteronuclear diatomics will feature as deformed ellipsoids, where the dispersion-induction centre would not coincide with the centre of mass. Larger diatomics or polyatomic molecules are better seen as a combination of ellipsoids (multiple dispersion-induction centres) defined in terms of contributions of molecular polarizabilities, associated both to each bond and to each lone pair [82]. It will be of great help to establish a formal phenomenology.

Ab initio and other computational methods are to be invoked to provide quantities such as the 'isodensity contour maps' of the HOMO orbitals of the electron donor and the LUMO orbitals of the acceptor. This theoretical information is necessary for a proper evaluation and modelling of V_{CT}.

Further relevant information that quantum chemistry is expected to provide is the charge distribution on the molecular structure. Recipes are becoming available for use in force fields of large molecules (see Ref. [83] and references therein). This is needed to define both V_{ELECTR} and the electric field in each point in space outside the distribution itself [77, 78]. The latter is required for the correct modelling of V_{IND}. Finally, *ab initio* and other computational methods can be of help in establishing if and how the relative role of various terms is changing while molecules undergo rearrangements in the field of the interaction potential [84a]. Our current efforts are involved in probing proper representations for V in systems containing closed-shell atoms or ions or metastable atoms, and polyatomic molecules [84].

Another interesting feature requiring additional investigations are the effects of the vibrational excitation (or of the molecular deformation) on the components of the polarizability tensor and on the distribution of charges. How these effects influence V is not well known, even in the case of simple diatomic molecules.

4.3. *From van der Waals interactions to chemical bonds*

In conclusion, the activity that we have reviewed in this field has prospects of continuing to yield further progress, possibly from the combined use of experimental and computational results, in order to fill the gap between the two extreme limits of interatomic and intermolecular interactions, ranging from weakly bound aggregates (van der Waals) to the strong chemical bonds. A suggestion is that the transition can be watched from indicators of the increasing role played by some electronic (single electron at lone pair) exchange or other type of 'sharing' such as that of a proton in hydrogen bonds: in the case of open-shell–open-shell interacting partners this finds its full realization in what is commonly referred to as a 'covalent' bond. Three examples of how this effect prototypically appears within the framework of this article are contributions to $V_{\mathrm{COV}} = V_{\mathrm{CT}} + V_{\mathrm{SS}}$ introduced in appendix B:

(i) *Stabilization by electron transfer*, amply documented in the rare-gas oxides and halides discussed in section 3.

(ii) *Spin–spin interaction* in the oxygen dimer. In [75] the O_2–O_2 case is discussed, where the spin–spin component adds to the anisotropic van der Waals term. It was found that near the equilibrium distance V_{SS} is of the order of ~15% of V_{VDW}. Reference [75] also reviews the venerable history of this case that has intrigued both Linus Pauling and G. N. Lewis as a peculiar type of a chemical bond.

(iii) *Proton sharing ('embryonic' hydrogen bond)*. The final example is provided by the water–noble-gas systems, for which the experimental determination (from molecular beam scattering) together with quantum chemical computational information have been compared to a phenomenological estimate of the V_{VDW} component [84c]. The comparison has yielded the quantification of the small – yet significant – effect of other interaction components responsible for the 'birth' of the hydrogen bond [84c].

Acknowledgements

We express our thanks to all our coworkers who have contributed in the past to the developments described in this article and whose names are associated to ours in the bibliographic references. Support from the Italian Ministry for Education, University and Research (MIUR) through PRIN and FIRB contracts is acknowledged.

Appendix A – Interatomic forces by molecular beam scattering

The intermolecular interaction potential V affects macroscopic as well as microscopic properties of the matter [77, 78]. In this appendix we briefly discuss those experimental observables providing relevant contribution to the knowledge of V, while particular emphasis will be addressed to the molecular beam scattering cross-sections which are the measurable quantities of many relevant experiments, such as those carried out in our laboratory.

The more traditional source of data comes from measurements on physical properties of gases, but very fruitful information is provided by high-resolution spectroscopic and scattering experiments [77, 78]. However, as a general consideration it should be stressed that since each experimental observable probes particular features of V, the simultaneous analysis of several experimental data of different nature is an important key to obtain an accurate characterization of the interaction potential over wide intermolecular distance and relative orientation ranges.

One of the classic source of data, sensitive to V, is the second virial coefficient $B(T)$, especially when measured in a wide temperature (T) range. Negative values of $B(T)$ (low temperature) are mainly affected by the attractive part of V, while positive $B(T)$ values (high temperature) are related to the repulsive region [77, 78]. The transport coefficients of a pure diluted gas – shear viscosity, thermal conductivity and self-diffusion coefficient – depend more indirectly on V. Therefore, they can be used to mainly gauge the validity of a given V, obtained from other methods. Transport properties (essentially, diffusion and mobility) of ions in the neutral gases and in presence of electric fields of arbitrary strength are again related to the ion–neutral interaction potential [85, 86]. Experiments on condensed phase can also provide information on V, but they are complicated by many-body effects [77, 78].

An important source of accurate data comes from spectroscopy and for an ample illustration of the range of applications see, for instance, Refs. [87–89]. In addition, the combined use of molecular beam and laser techniques offers further advantages because of increased resolution conditions. Several systems, involving molecular partners, have been spectroscopically investigated and accurate potential energy surfaces obtained. Some cases relevant to this article are Rg–HCl [90], Ar–H_2O [91] and H_2O–H_2O [91], H_2–Rg and H_2–H_2 [92], HF–HF and N_2–HF [93], Ar–C_2H_2 [94a, 94b], Ar–C_2H_4 [94c] and Rg–C_6H_6 systems [95]. Because of difficulties in preparing the aggregates of interest, spectroscopic investigation on weakly bound atom–atom systems are more limited (see for example Refs. [56b–56g]. An important contribution has been furnished by ‘zero electron kinetic energy spectroscopy’ [96, 97]. However the largest body of information has been provided by scattering experiments. Usually, they are performed using the molecular beam technique [98] and measuring either differential or integral cross-sections. The integral cross-section experiment consist in the measurement of the attenuation of a velocity selected beam (see figure 9) by a target contained in a scattering chamber. A two beams configuration is used for differential cross-section measurements (see figure 9), where the intensity of the particles scattered at various angles is monitored by a rotating detector.

For the accurate characterization of the interaction potential features it is necessary to use high-resolution conditions both in energy and in angle, in order to measure interference effects, such as the glory structure in integral cross-sections or rainbow and diffraction oscillations in differential cross-sections (see figure 10). Two examples of integral cross-section experiments are reported in figure 11 (see also Ref. [70c]).

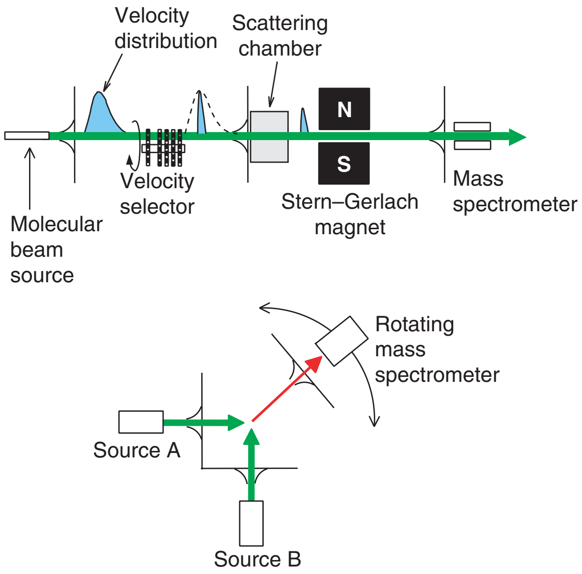

Figure 9. Sketch of the experimental techniques used to measure integral (top) and differential (bottom) cross-sections.

Measurements have been carried out using Ar or O_2 beams scattered by Kr under the same conditions. The obtained results demonstrated that when O_2 is rotationally 'hot' it behave similarly to Ar.

In systems involving open-shell atoms or molecules the anisotropy of the interaction can appreciably modify the measured cross-sections, with quenching and shifting of the interference partners. These effects are useful for obtaining detailed information on the full interaction through the analysis of scattering data, but they are often hard to unravel. The use of polarized atomic and molecular beams in scattering experiments is therefore crucial for the characterization of both the collision dynamics and the interaction potentials.

In the case of beams of open-shell atoms the selective deflection analysis, obtained by a Stern–Gerlach magnetic selector, allowed us to measure and to control the magnetic sublevel populations in the atomic beams [99]. The magnetic analysis drives the collision along adiabatic potential curves of defined symmetry (appendix C). In the case of molecular beams, collisional alignment of the rotational angular momentum **J** (corresponding to defined **J** projections with respect to the beam propagation directions) can be naturally induced during the beam formation. Magnetic [100], scattering [101] and laser absorption [102] techniques have been used to probe the molecular alignment degree and pronounced effects are observable when mixtures containing molecules in excess of lighter seeding gases are used and a proper velocity selection is implemented. Scattering experiments with polarized atomic and molecular beams permitted us to obtain information on the anisotropic interactions presented in sections 3 and 4, respectively.

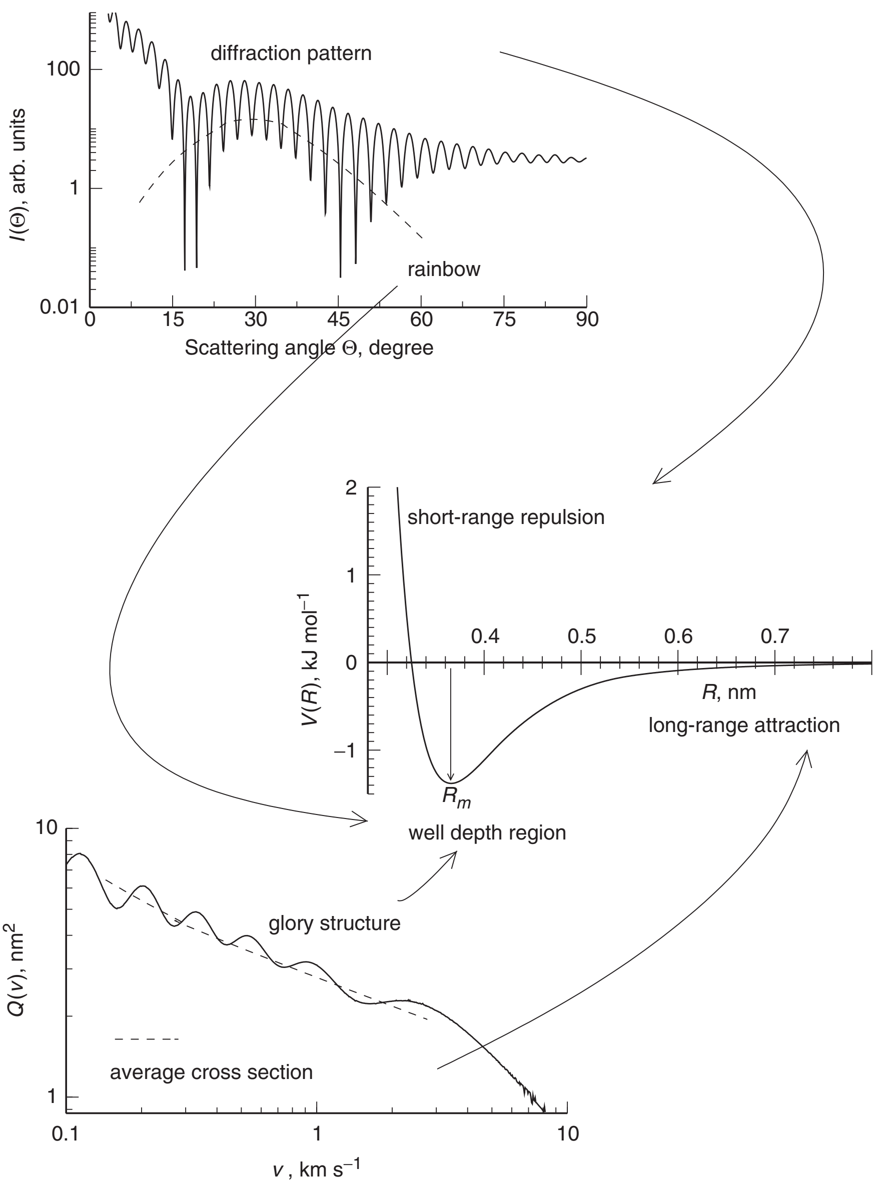

Figure 10. Specific features of the intermolecular potential obtainable from the analysis of the scattering results are indicated. Simulations are performed with the potential reported in the intermediate panel and considering a system with a reduced mass of 0.018 kg mol^{-1}.

Appendix B – Basic contributions to the interatomic interactions and their dependence on physical properties of involved species

Alternative partitions of V can be proposed from different viewpoints (see for instance Ref. [103]) which may converge only at sufficiently long range for a perturbation theory

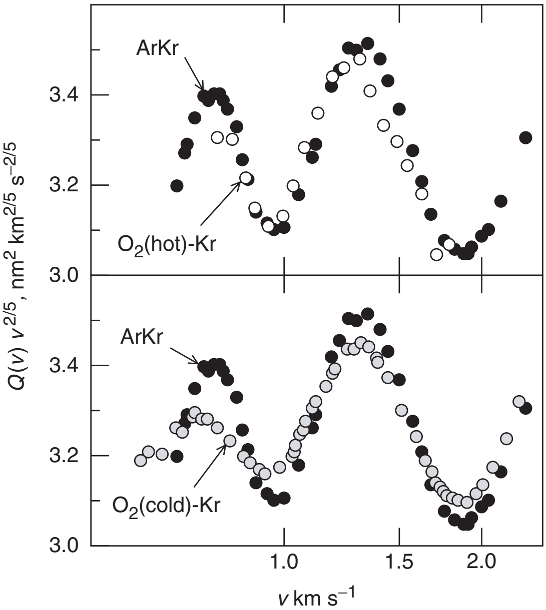

Figure 11. Integral cross-section for scattering of Ar and O_2 beams by Kr target, measured as a function of collision velocity *v*. To emphasize the glory structure, the cross-sections *Q* are multiplied by $v^{2/5}$. Data for O_2 scattering have been measured with oxygen molecules, rotationally 'cold' and rotationally 'hot', to show the behaviour as molecular or spherical projectile at low and high temperature, respectively. For more details see [70c].

treatment to be appropriate. In the present approach we observe that many of the higher order contributions to V often provide opposite effects and tend to cancel out so that we will consider only a few leading components of the interaction, to be taken as *effective* terms. They scale in a different way with the distance between the interacting partners. Interestingly, ranges and strengths of these effective components are amenable of experimental investigation in the case of some prototypical system. We aim also at developing appropriate functional representations in terms of basic physical properties of the interacting particles.

We choose the following partition of V, in part adhering to current customary expressions (e.g. Refs. [87, 88]) and including what is needed in the discussion in the main text:

$$V = V_{\mathrm{REP}} + V_{\mathrm{DIS}} + V_{\mathrm{IND}} + V_{\mathrm{ELECTR}} + V_{\mathrm{CT}} + V_{\mathrm{SS}} \tag{17}$$

Here, all terms depend on R, the intermolecular distance, and on the relative orientation of more external orbitals of any of the two interaction partners. V_{REP}, V_{CT} and V_{SS} dominate at short distances and die quickly, as R increases, while the other terms start to enter into play. Their delicate balance produces the potential well, whose energy and location ε and R_m are the most important measure of strength and range of the interaction $V(R)$.

The first four terms in (17) determine the typical 'non-covalent' interaction for which the appropriate nomenclature uses names like 'ionic', 'van der Waals', etc.

The V_{CT} and V_{SS} terms, arising respectively from charge-transfer and spin–spin coupling, play the role of additional basic components. They represent those contributions to the interaction which, in those cases where there is very limited electron exchange and electron sharing between the two partners, can be considered as examples of manifestation of (embryonic) 'chemical' bonds. Their combination is designated as

$$V_{\mathrm{COV}} = V_{\mathrm{CT}} + V_{\mathrm{SS}} \tag{18}$$

Experience shows that these terms can be correlated to relatively few physical properties of the separated species (this discussion is focused on atoms, but many features hold for molecules as well). We list the physical properties, again in order of appearance on the scene from left to right in equation (17):

- The (static) polarizability α, which accounts for the second order response of the species to an electric field. Chemists have for a long time associated this quantity to concepts such as 'softness' or to the inverse of 'molecular hardness'. It is also empirically correlated to the inverse of the HOMO-LUMO difference of a molecular system. London [104] established how α correlates with tendency of a systems to get excited, or somehow 'deformed' through the formation of induced multipoles (typically dipoles). Since the polarizability of a conducting sphere coincides with its volume (see e.g. Ref. [105]), α also describes the spherical region within which the species gets polarized and thus represents its 'size', i.e. the space that it occupies [106, 107].
- The total charge q of relevance for ions and the distribution of partial charges, which define the electric field around a species.
- The ionization potential of an electron donor I_{D} and the electronic affinity of an electron acceptor A_{A}, which define the capability for a donor to lose an electron and for an acceptor to catch it. These two quantities contribute to the definition of the radial behaviour (typically exponentially decreasing with R) of the orbital from which the electron leaves and of the orbital which describes the final state of the electron after the jump: I_{D} and A_{A} measure the energies of these orbitals.
- Spin and orbital angular momenta **S** and **L** (we typically deal with atoms in LS coupling but see appendix C), which are of importance in open-shell species and depend on the electron distribution in valence orbitals.

Let us now examine the various terms in (17) in the light of the role played by the above ingredients.

V_{REP} This repulsive contribution is dominated by electron cloud dimensions and short-range exchange effects and is extremely difficult to obtain quantitatively from an *ab initio* or other quantum chemical approaches. It depends on the 'size' of the outer orbitals and in the range where orbital overlap is not yet extensive it can be conveniently correlated with the polarizabilities of the partner [106].

V_{DISP} The dispersion (London) term arises from instantaneous mutual polarizations which each partner induces on the other. It has long been known that it correlates with the product of their polarizabilities and the leading term scales as R^{-6}.

V_{IND} Induction terms account for polarization effects that the charge distribution on one of the partners induces on the other. For an atomic ion, considered as a point charge, and a neutral whose polarizability is α,

$$V_{\mathrm{IND}} = -1/2\alpha q^2 R^{-4},$$

the Langevin ion-induced dipole term.

V_{ELECTR} This is simply the Coulombic interaction between the permanent charge distributions of the two species. At distance R large enough with respect to their average dimensions one has to add to the R^{-1} term, describing the interaction between total charges, those depending on permanent multipoles [87, 88].

V_{CT} The charge-transfer (or charge-exchange) contribution involves an electron donor D and an electron acceptor A. It is one of the hardest quantities that quantum chemistry may ever have to tackle. The crucial parameter for its discussion is typically denoted H_{AD}, and called 'charge-transfer coupling'. Its importance decreases with the difference in energy ΔE between the states of the systems before and after the electron jump. At large and intermediate distances (R close to the equilibrium distance), H_{AD} is proportional to the overlap integral $\mathcal{S}$ [108] between orbitals exchanging the electron. Therefore, H_{AD} decays exponentially as R increases and depends on I_{D} and A_{A}. Various correlation formulas have been proposed for H_{AD}, all of them of the general form [109–113]

$$H_{\mathrm{AD}} = CR\exp\left[\left(\frac{I_{\mathrm{D}}^{1/2} + A_{\mathrm{A}}^{1/2}}{2^{1/2}}\right)R\right] \tag{19}$$

where in (19) R is in atomic units. Two limiting cases are of interest:

(i) $I_{\mathrm{D}} = A_{\mathrm{A}}$ (resonant charge-exchange), then, one has simply $V_{\mathrm{CT}} = H_{\mathrm{AD}}$. Since H_{AD} is negative, this is a contribution to the attraction – a stabilization of the bond.

(ii) $I_{\mathrm{D}} \gg A_{\mathrm{A}}$ (non-resonant charge-exchange), then, it is proposed that $V_{\mathrm{CT}} = H_{\mathrm{AD}}^2/\Delta E$ according to pertubative treatment. The knowledge of I_{D} and A_{A} values permits to anticipate relevant features of H_{AD}. In the text an indirect method to obtain the C value is also discussed.

V_{SS} The spin–spin term decays exponentially with R since depending again on the orbital overlap. It strength varies also with the total spin angular momentum value of the electronic state.

Appendix C – Electronic anisotropy and orbital alignment

Treatments of the collision dynamics in presence of open-shell effects exploit the classification of rotational spectra of diatomic molecules according to alternative coupling schemes of the involved angular momenta. A collision is seen as a sequence of such schemes, analogous in the spectroscopy of diatomic molecules to the five Hund's cases, leading to the quantum mechanical formulation of alternative coupling schemes for the description of collisions between atoms having non-zero internal spin and or electronic angular momenta. This appendix presents a brief account of the corresponding diabatic representations and of the orthogonal transformations among cases, also of relevance for a description of the interactions in terms of isotropic and anisotropic contributions.

Hund's classification of rotational states of diatomic molecules [114] has inspired the description of collisional fine structure and polarization (alignment and orientation) effects as a transition between an atomic picture at long range and a molecular one at short range. The semiclassical formulation by Nikitin and others [115], who developed the theory in terms of alternative couplings of the involved angular momenta, employed the simplifying assumption of classical nuclear motion.

The full quantum mechanical formulation [116] permits the localization of transitions between angular momentum coupling schemes, and the development [117] of decoupling approximations in limiting cases: such decoupling imply selection rules [118] for intramultiplet mixing and polarization (alignment and orientation) transfer cross-sections. For earlier work, see [119].

Recent developments in molecular beam and laser techniques have fostered the extension of the scope of earlier treatments, particularly with reference to orbital alignment upon collisions and to the concept of a transition (or orbital locking) radius [120, 121]. Further interest comes from ultracold atomic collision problems [122], which also inspired a formal extension to deal with the general case of two interacting open-shell atoms [123]. In our view of atom–atom interactions, the transition radius R_x separates two regions where the system can be described as 'diatom' ($R \leq R_x$) or as a 'molecule' ($R \geq R_x$). This depends on angular momentum **J** (rotational, if one thinks in spectroscopic terms, or orbital, if one thinks of a collision experiment).

The theory developed in Ref. [116] introduces five alternative representations for the quantum mechanical close coupling ('exact') formulation of both the motion along the intermolecular distance of a vibrating diatomic molecule and the dynamics of colliding atoms having internal (spin and/or orbital) angular momenta. The multichannel Schrödinger equation in matrix form reads, at a given total angular momentum,

$$\left[\left(\frac{\hbar}{2\mu}\frac{d}{dR^2}+E\right)\mathbf{1}-\boldsymbol{V}^{\mathbf{D}}(R)\right]\mathbf{u}(R)=0 \tag{20}$$

where E is the collision energy and μ is the reduced mass of the couple of atoms. When fine structure states are explicitly introduced in the close coupling expansion, the effective potential $\boldsymbol{V}^{\mathbf{D}}$, whose off-diagonal matrix elements provide the coupling for

(19), can be considered as the sum of three terms:

$$\boldsymbol{V}^{\mathbf{D}}(R) = \left(\Delta + \frac{\hbar^2 J^2}{2\mu R^2}\right)\mathbf{1} + \boldsymbol{U}_{\mathbf{INT}} \tag{21}$$

representing spin–orbit, rotational, and interatomic interactions $\boldsymbol{U}_{\mathrm{INT}}$, respectively. Note that the effective potential is now a *diabatic* matrix ($\boldsymbol{V}^{\mathbf{D}}$) representative of the interaction in one of the alternative basis, are no more a scalar as in the text. The five alternative representations, motivated by the relative importance of the three terms in (21), correspond to alternative coupling schemes and Ref. [120] outlines their geometrical significance, according to a sequence of four vector coupling schemes.

The prime importance of the relative values of the three terms, which in general have a markedly different R dependence, is clear from (21). The spin–orbit splitting in the multiplet, Δ, is approximately constant at long range and typically varies much less than the centrifugal, which goes approximately as J^2/R^2, while the anisotropy of the electrostatic interaction, of relevance for the term V_{CT} in this discussion, drops exponentially with R. Consider a P-state atom ($L=1$): the isotropic and anisotropic components in this article (section 3) can be defined in terms of the proper sums and differences of the 'spectroscopic' potentials (the symbol Σ denotes as usual $\Lambda=0$ states, while Π means $\Lambda=1$ where Λ are absolute projections of $\mathbf{L}$ on the interatomic distance vector R):

$$V_0 = \frac{1}{3}(V_\Sigma + 2V_\Pi) \tag{22}$$

$$V_2 = \frac{5}{3}(V_\Sigma - V_\Pi) \tag{23}$$

Modifications for $L > 1$ are obtained enforcing the harmonic expansion of electronic anisotropy [116].

In Refs. [53, 117], we gave explicit examples of the coupling case sequence in the limit of large and small spin–orbit splitting. In the case of large Δ, the transition between 'diatomic' and 'molecular' coupling schemes, as measured by maxima in non-adiabatic coupling matrix elements takes place among states having the same projection ω of the electronic angular momentum $\mathbf{J}$ on the molecular axis: it varies slightly with ω, as exemplified by the open-shell–rare-gas systems [58] discussed in section 3. The opposite situation, i.e., no (or negligible) spin ($\Delta \cong 0$ in (23)), can be formulated similarly, and applies, e.g. to excited alkali noble gas systems, see Ref. [55].

In Ref. [116] we also show that for a ^{2}P-state atom interaction with a closed-shell systems (a three-channel problem) no coupling or recoupling occurs for one state fully decoupled by parity, while for the other two states the transition radius can be defined semiclassicaly

$$R_x = \hbar\left[\frac{2(J + (1/2))}{\mu(V_\Sigma - V_\Pi)}\right]^{1/2} \tag{24}$$

This formula is seen to be identical to that in Ref. [116], where a collisional viewpoint is adopted, the correspondence being $\hbar(J+(1/2))=\mu v\ b$, where v is the velocity and b is the impact parameter: an interatomic distance $R>R_x$ or $R<R_x$ corresponds to ranges of validity for atomic or molecular angular momentum coupling schemes, respectively.

This analysis can be made more precise within the full quantum mechanical framework. The various alternative representations of (20) are *diabatic*, being the coupling embedded in the effective potential $U(R)$ (21) and the transformation between cases being independent of R. An adiabatic representation

$$\left[\frac{\hbar^2}{2\mu}\left(\mathbf{1}\frac{d}{dR}-\mathbf{P}\right)^2+E\mathbf{1}-\boldsymbol{V}(R)\right]\mathbf{u}^A(R)=0 \tag{25}$$

is obtained by an R-dependent orthogonal transformation, say $\boldsymbol{T}(R)$, which diagonalizes $\boldsymbol{V}^{\mathbf{D}}$ yielding the adiabatic effective potentials.

$$\boldsymbol{V}(R)=\tilde{\boldsymbol{T}}\boldsymbol{V}^{\boldsymbol{D}}\boldsymbol{T} \tag{26}$$

and the skew symmetric coupling matrix

$$\boldsymbol{P}=\tilde{\boldsymbol{T}}\boldsymbol{T}' \tag{27}$$

Here the tilde indicates transposition and the prime differentiation with respect to R. Now $\boldsymbol{V}(R)$ is a diagonal matrix, each scalar eigenvalue is an effective interaction potential, their manifold corresponding to the set indicated V in the open-shell cases of section 3. Explicit expressions in terms of V_0, V_2 and Δ (or V_Σ, V_Π and Δ) are, e.g. in Ref. [53].

While it is impossible to define a unique distance which marks the transition (which varies with J), it appears useful to discuss within this theory the concept of orbital locking and unlocking during the collision, which is a concern of much work [120–124]. Experimentally, orientation and alignment of angular momenta are prepared for reactants or measured for products with respect to polarization axes defined by the experiment, while the driving forces for the collision are a function of the internuclear axis: transformation from space-fixed to body-fixed frames usually provide only a superposition of orbitals having a distribution of angular momenta and their projections along the internuclear axis. Only at short range (cases a and b of Hund) does orbital symmetry become meaningful, when it is so large that quantum numbers Σ or Π are 'good' and can be taken as a label for orbital locking.

Further perspectives on these problems open up when one goes beyond the adiabatic representation to build up *post-adiabatic* potentials [125]. Most examples treated so far deal with those of section 3, but their discussion is outside the scope of this article.

An approach similar to the previous one for orbital orientation can be formulated also for the quantum mechanical definition of oriented and aligned molecular states. We can follow a route analogous to the above sequences of Hund's cases exploiting frame transformation theory from space- or body-fixed systems and a discretization procedure [126] for the continuous relative orientation between molecular axes and collision direction, so that it becomes possible to obtain appropriate angular momentum coupling schemes and decoupling approximations, as exemplified in [126] for closed-shell atom–molecule interactions. New steric quantum numbers emerge to label molecular orientation [127] and to solve the multichannel Schrödinger equations (20) or (25) not only for inelastic but also for reactive scattering [128]. Indeed, most chemical reactions are triggered by open-shell effects in entrance channels (atoms or radicals attacking molecules) and lead to products also possibly having open-shell characteristics. Therefore electronic anisotropy is an important issue to be addressed in the formulation of potential energy surfaces of most chemical reactions and in the study of their dynamics. Examples of their treatments in the spirit of this article for prototypical species, such as the reactions of ^{2}P halogen atoms (F, Cl) with simple molecules, are provided by Ref. [129]. For transport properties, see [130]. In energy transfer processes [131], ion–molecule reactions [132] and ion–ion recombinations [133], account has to be taken also of non-adiabatic coupling to charge-exchange excited states.

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