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# THE EFFECTS OF COLLISIONS ON MOLECULAR PROPERTIES

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Abstract - This lecture is concerned with the changes in molecular properties that result from intermolecular forces. In addition to the potential energy, the optical, electric and magnetic properties of molecules, as well as transition probabilities, may change as a result of collisions. Some properties, such as simultaneous transitions and the circular dichroism of an achiral solute in a chiral solvent, result entirely from the interaction.

In the general theory of the effects of long-range intermolecular forces on molecular properties, the change is expressed in terms of properties of the free molecules. The usefulness and limitations of such a description are considered. Progress in understanding intermolecular forces and solvent effects will depend upon a combination of experiment, ab initio computation and simulation.

## INTRODUCTION

The environment of a molecule may have a profound effect upon its physical and chemical properties. To illustrate the point I shall show you the fluorescence of a non-ionic dye, dimethylnaphtheurhodine, in a series of eight solvents. The emission ranges from blue in n-hexane to red in methanol.

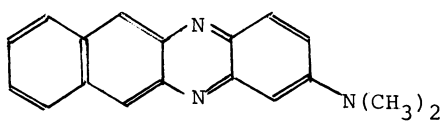


Fig. 1. Dimethylnaphtheurhodine, a non-ionic dye showing fluorescence at different wavelengths when dissolved in $CH_3OH$, $C_2H_5OH$, $(CH_3)_2CO$, $CHCl_3$, $(C_2H_5)_2O$, $C_6H_6$, $CCl_4$, and n-hexane. I am very grateful to Dr. E.J. Bowen, F.R.S., of Oxford for loaning these solutions for display at this Symposium.

Measurements of changes in the emission and absorption spectra of solutes with the solvent and with temperature have been used by Lippert (1), Liptay (2), and others to deduce changes in the charge distribution in the solute in its ground and excited states. However, the results are dependent on the applicability of simple models, and in particular the 'reaction-field' model of Onsager (3), in which the surroundings of the solute (which is assumed to be spherical) have the bulk properties of the fluid. Such results, and indeed most that relate to properties of a molecule in a condensed phase, should be treated with caution. Measurements of optical and electric properties of solute molecules are often of doubtful validity because the relationship between the observable and the molecular property is model-dependent. However, in gases it is possible to determine rigorously the effect of collisions on properties. Much of this lecture is therefore concerned with interacting pairs of molecules, and how the properties of a pair may differ from those of two non-interacting molecules.

What are the effects of molecular collisions on the properties of molecules and of bulk matter? The question is central to this conference. It was also the subject of a part of the First International Congress of Quantum Chemistry in 1973 (4) and of the Eighth Jerusalem Symposium on Quantum Chemistry and Biochemistry in 1975 (5). While much is known (and much unknown) of intermolecular forces, which arise from changes in the *potential energy* of the

system as a result of the interaction of molecules, much less is known of the corresponding changes in molecular *properties*, such as optical, electric and magnetic properties and transition probabilities. The point is illustrated by Fig. 2 which shows the familiar interatomic potential energy $u_{12}$ for a pair of inert-gas atoms as well as the mean polarizability $\alpha_{12}$ and polarizability anisotropy $\Delta\alpha_{12}$ of the same pair of atoms. The potential has a single minimum

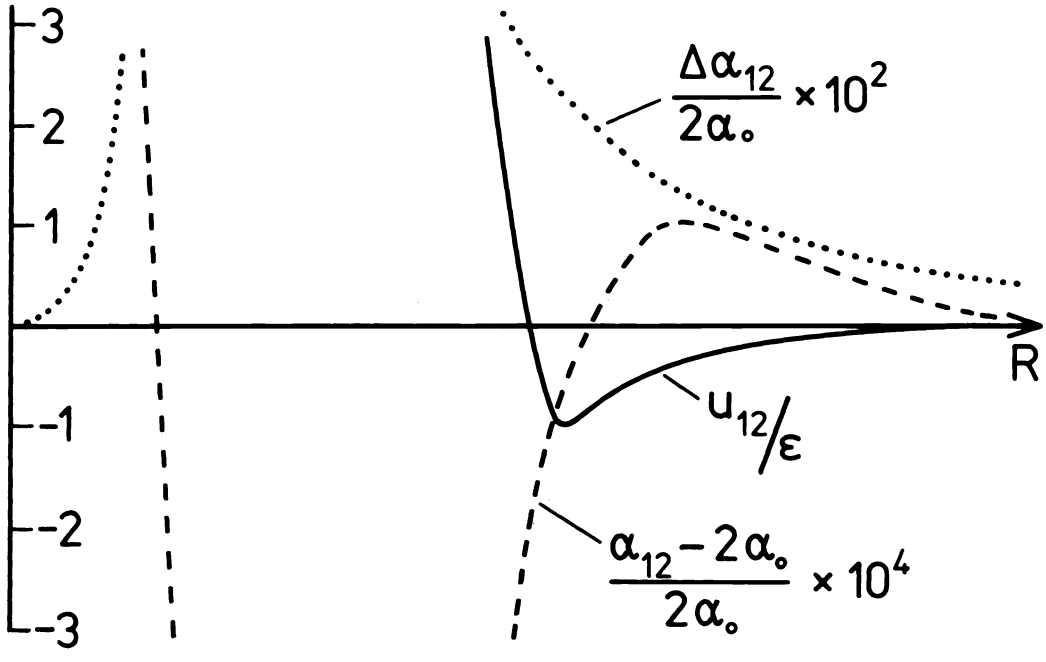


Fig. 2. The potential energy $u_{12}$, the mean polarizability $\alpha_{12} = \frac{1}{3}(\alpha_{\parallel} + 2\alpha_{\perp})$, and the polarizability anisotropy $\Delta\alpha_{12} = \alpha_{\parallel} - \alpha_{\perp}$ for a pair of inert-gas atoms, as a function of their separation R. $\varepsilon$ is the well-depth of the potential and $\alpha_0$ the polarizability of an isolated atom.

of depth $\varepsilon$ at $R = R_e$, but the mean polarizability has a maximum at approximately 1.2 $R_e$ and a deep minimum at about 0.5 $R_e$. The long-range interactions lead to an increase in $\alpha_{12}$ that varies as $A_6R^{-6} + A_8R^{-8} + \ldots$ at large R (6,7). $A_6$ and $A_8$ are positive and result from the classical field and field-gradient at one atom due to the dipole induced in the other atom, and from the distortion associated with the long-range dispersion forces; the latter is dominant for H + H and He + He, but the classical term increases in importance on going to heavier atoms and accounts for about two-thirds of $A_6$ in Xe + Xe (7). The anisotropy $\Delta\alpha_{12}$ is dominated by the long-range dipolar contribution in $R^{-3}$:

$$\Delta\alpha_{12} = (\alpha_{\parallel} - \alpha_{\perp})_{12} \simeq \frac{6\alpha_0^{(1)}\alpha_0^{(2)}}{(4\pi\varepsilon_0)R^3} + \Delta A_6 R^{-6} + \Delta A_8 R^{-8} + \ldots \qquad (1)$$

The 'short-range' forces resulting from electron overlap and exchange tend to reduce $\Delta\alpha_{12}$ and to make $\alpha_{12} - (\alpha_0^{(1)} + \alpha_0^{(2)})$ negative (Refs. 8,9), thereby yielding a maximum in $\alpha_{12}$ (see Fig. 2). This maximum occurs at sufficiently large R to make the mean change in $\alpha_{12}$ negative for He + He and Ne + Ne, although it is positive for Ar + Ar and Kr + Kr at normal temperatures (10-12). The intensity and frequency-dependence of collision-induced light scattering provides a means of measuring $\Delta\alpha_{12}$ (13); the topic has recently been reviewed by

Frommhold, who concludes that the $R^{-3}$ contribution in equation (1) is generally sufficient for an accurate account of the scattering by compressed inert gases (14).

The overlap effects on molecular properties are normally represented empirically. For example it is often sufficiently accurate to suppose that

$$p(R) = p_{\ell r}(R) - \lambda \exp(-R/R_0) \qquad (2)$$

where $p_{\ell r}(R)$ is the long-range contribution to the property $p$, $R_0$ is a distance which is of the order of 0.1 $R_e$, and $\lambda$ is a measure of the strength of the short-range effect. Note that the short-and long-range effects are generally of opposite sign.

At very small separations there are large changes in $\alpha_{12}$ and $\Delta\alpha_{12}$ due to 'united-atom' effects. Thus as $R \to 0$, $He_2$ becomes Be which has a $1s^2 2s^2$ ground configuration and is approximately 13 times as polarizable as 2He (15). Since the atom is spherical, $\Delta\alpha_{12} \to 0$ as $R \to 0$. However, these very short separations are not of practical interest since they are forbidden by the enormous repulsion.

When diatomic and polyatomic molecules collide, there are other causes of change in the polarizability, and these are considered in the next section.

Just as intermolecular forces vary greatly in their strength - from the weak forces between inert-gas atoms, through electrostatic forces and the hydrogen bond, to chemical interactions - so too do the corresponding property changes $\Delta p$. In this lecture we are concerned with molecules whose identity is retained, although there can be changes in bond lengths and angles, as well as electronic effects. There may be transfer of electrons at short-range, so that the property (the dipole moment, for example) belongs to the interacting group of molecules rather than being partitioned among the individuals. If we were to consider the collision of two molecules containing $N_1$ and $N_2$ atoms, the property surface $p(\underset{\sim}{R}_{N_1}, \underset{\sim}{R}_{N_2})$ depends on $3(N_1 + N_2) - 6$ independent variables (except for $N_1 = N_2 = 1$, for which the number of variables is one - the separation R) (16). If other molecules are present, we could average over their positions and orientations to obtain an average property surface $p(\underset{\sim}{R}_{N_1}, \underset{\sim}{R}_{N_2}, T)$ which would be a function of the temperature T. Thus there are six degrees of freedom for two diatomics ($R$, $\theta_1$, $\theta_2$, $\phi$, $r_1$, $r_2$, where $r_1$ and $r_2$ are the intramolecular distances in diatoms 1 and 2), and twelve for two triatomics, such as the water dimer $(H_2O)_2$. If we overlook internal degrees of freedom, there are in general six variables describing the relative position and orientations of two polyatomic molecules, $p(R, \underset{\sim}{\Omega}_1, \underset{\sim}{\Omega}_2)$, but such a reduction would obviously not be appropriate if we were interested in a vibrational effect such as solvent influences on infrared and Raman intensities. Any practical description of the interaction of large molecules must focus on a small number of internal degrees of freedom, such as an angle of internal rotation or a single mode of vibration, apart from position and orientation.

Some properties are due entirely to the interaction - for example the dipole moment $\mu_{12}$ of a pair of dissimilar atoms, $\mu_{123}$ for three identical atoms, the anisotropy in polarizability $\Delta\alpha_{12}$ of inert-gas atoms, circular dichroism at the absorption frequency of an achiral solute in the presence of a chiral solvent (17), and simultaneous vibrational transitions in two molecules (18).

## POLARIZABILITY

The polarizability of a pair of interacting atoms has already been discussed. We now consider the case of molecules, and classify the changes under five headings:

(i) Classical dipolar interaction leads to the $R^{-3}$ term in equation (1). It has been invoked to explain molecular polarizabilities in terms of additive atomic contributions (19) and hence to interpret vibrational Raman intensities and optical activity (20).

(ii) Intrinsic changes in $\alpha$ due to dispersion forces increase the magnitude of $A_6$ in the long-range polarizability expansion over its classical value by factors of 4.7 for H + H, 3.7 for He + He (6), and by lesser

amounts for heavier atoms (7).

(iii) Short-range overlap interactions reduce $\alpha_{12}$ and $\Delta\alpha_{12}$ for atoms and cause the negative second dielectric virial coefficients of He and Ne.

(iv) Non-linear polarization in the presence of strong electric fields from the non-spherical charge distribution of neighbouring molecules. Such an effect is related to the first hyperpolarizability of the molecule and to the electric multipole moments of the neighbour. It has been suggested as a mechanism for collision-induced Raman scattering (21, 22).

(v) Non-uniform fields acting on higher polarizabilities can yield fluctuatin dipoles. Thus a field-gradient $F'_{\beta\gamma}$ acts on the dipole-quadrupole polarizability $A_{\alpha\beta\gamma}$ to induce a dipole $\mu_\alpha = \frac{1}{3} A_{\alpha\beta\gamma} F'_{\beta\gamma}$. This dipole is modulated by rotation and vibration and can be the dominant contribution to collision-induced scattering (23-25). There is just one independent component of $\underset{\sim}{A}$ for a tetrahedral molecule and its role in collision-induced rotational Raman scattering is illustrated in Fig. 3. The field-gradient comes from the dipole $\alpha^{(2)}\underset{\sim}{F}$ induced in a neighbour by the optical field, so $F'_{\beta\gamma}$ is proportional to $\alpha^{(2)}R^{-4}F$. The corresponding change in $\alpha_{12}$ is proportional to $A^{(1)}\alpha^{(2)}R^{-4}$ and is analogous to the familiar term in $\alpha^{(1)}\alpha^{(2)}R^{-3}$ in equation (1).

(vi) Distortion of the molecular structure by the collision is normally a minor contribution to induced scattering (26), but if a vibrational mode is soft, or the translational energy high, there could be significant changes in structure and hence of $\alpha_{12}$.

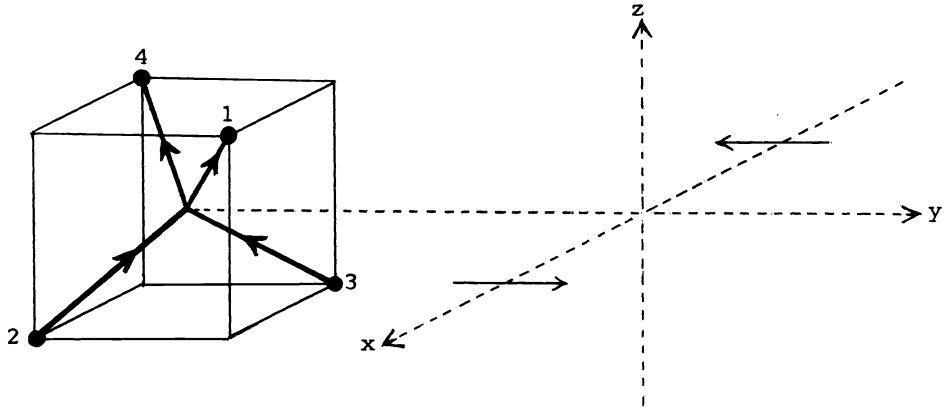


Fig. 3. A tetrahedral molecule in a field gradient $F'_{xy}$. The anisotropic polarizability of the four bonds contributes positively to the induced dipole $\mu_z$. Bonds 1 and 2 have a positive displacement along the x axis and therefore experience a positive field $F_y$, while bonds 3 and 4 are in a negative $F_y$. If $\alpha_{\parallel} - \alpha_{\perp}$ is the anisotropy of the polarizability of each bond located at a distance $r_0$ from the centre, $\mu_z = \frac{4}{3\sqrt{3}}(\alpha_{\parallel} - \alpha_{\perp})r_0 F'_{xy}$ so that $A = A_{zxy} = \frac{4}{\sqrt{3}}(\alpha_{\parallel} - \alpha_{\perp})r_0$. The induced dipole may rotate once, twice or three times for a rotation of the molecule (because of the $C_1$, $C_2$ and $C_3$ rotational axes in a molecule of $T_d$ symmetry), giving selection rules $\Delta J = \pm 1, \pm 2, \pm 3$ for the collision-induced rotational scattering (23).

Figure 4 shows an interferometer designed to measure differentially the changes in $\alpha$ resulting from collisions in the gas phase (27).

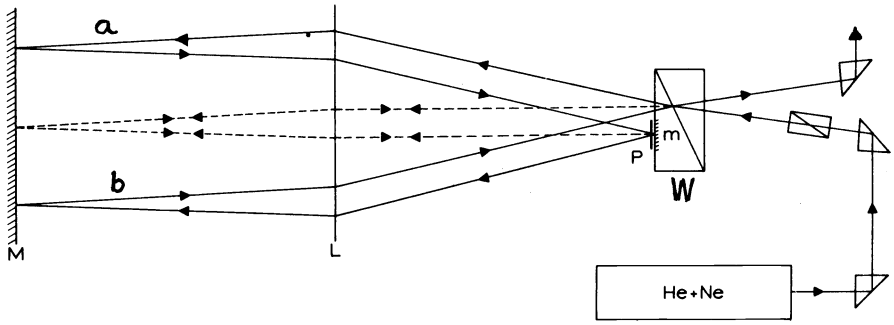


Fig. 4. A stable interferometer for measuring changes in polarizability due to collisions. M and m are mirrors, L is a lens and P a quarter-wave plate. The Wollaston prism W splits the incoming beam into two orthogonally polarized beams. The upper path *a* is through a gas in a tube at density ρ and the lower path *b* is through a similar empty tube. The central reference beams traverse air. A valve connects the two tubes and the final gas density is ½ρ in both. The change in the optical path is measured as an ellipticity in the emerging beam and it arises entirely from the collisions (27).

The hyperpolarizabilities of molecules, which are responsible for non-linear optical properties, are sensitive to the outer reaches of the electron clouds and are therefore probably more vulnerable to changes on collision. However, little is known of such effects, although electric-field-induced second-harmonic generation has been detected in gases (28, 29) and liquids (30).

## DIPOLE MOMENTS

Measurements of the electric dipole moments of van der Waals molecules, such as ArHF, ArHCl, $(HF)_2$, $(H_2O)_2$ (Ref. 31-33) can be compared with the dipole moments of the monomers. Thus the dipole moments of ArHCl and ArDCl are 0.81 and 1.00 D in the direction of the inertial axis (approximately the Ar...Cl direction) (Ref. 31) compared with $\mu_{HCl}$ = 1.1085 and $\mu_{DCl}$ = 1.1033 D (Ref. 34). These differences can be accounted for by considering the dipole induced in the argon atom by the field from the charge distribution of the HCl and the zero-point bending motion (Ref. 31).

The mean-square dipole moment of a pair of interacting molecules can be measured through the dependence of the permittivity ε on the density ρ.

$$\frac{\varepsilon-1}{\varepsilon+2}\rho^{-1} = A_\varepsilon + B_\varepsilon \rho + C_\varepsilon \rho^2 + \ldots \tag{3}$$

$A_\varepsilon$, $B_\varepsilon$, $C_\varepsilon$, ... are the first, second, third, ... dielectric virial coefficients and are functions of T (Ref. 35).

$$A_\varepsilon = \frac{4\pi N}{3(4\pi\varepsilon_0)}\left(\alpha_0 + \frac{\mu^2}{3kT}\right) \tag{4}$$

where N is Avogadro's number if ρ is in moles per unit volume. $A_\varepsilon$ is the contribution the molecules would make to the Clausius-Mossotti function if each were independent. $B_\varepsilon\rho$ is their <u>extra</u> contribution due to pairwise interactions and

$$B_\varepsilon = \frac{4\pi N^2}{3(4\pi\varepsilon_0)}\int\left[\tfrac{1}{2}\alpha_{12} - \alpha_0 + \frac{1}{3kT}\left(\tfrac{1}{2}\mu_{12}^2 - \mu^2\right)\right]\exp\left(-u_{12}/kT\right)dv_2 \tag{5}$$

The integration is over the positions and orientations of molecule 2 in a large spherical volume centred on molecule 1. Since $\mu_{12} = \mu = 0$ for monatomic gases, $B_\varepsilon$ is for them a measure of the mean change in polarizability. For gases such as $H_2$, $CO_2$, $CH_4$, and for mixtures of inert gases (e.g. Xe + Ar), $\mu = 0$ but $\mu_{12} \neq 0$ and the $T^{-1}$ term contributes to $B_\varepsilon$. For $CO_2$ at normal temperatures, $B_\varepsilon$ is dominated by this induced-dipole contribution (Ref. 36). To a useful approximation, $\mu_{12}$ can be equated to the dipoles induced by the fields of the neighbour:

$$(\mu_{12})_\alpha = \alpha^{(1)}_{\alpha\beta} F^{(12)}_\beta + \alpha^{(2)}_{\alpha\beta} F^{(21)}_\beta \tag{6}$$

where $F^{(12)}_\beta$ is the β-component of the field at the centre of molecule 1 due to the charge distribution of 2. $F^{(12)}_\beta$ can usually be adequately represented by the field of the first non-vanishing multipole moment of molecule 2 (Ref. 37-39). The intensities of collision-induced rotation—translation spectra (Ref. 40) have been used to deduce values for some of these multipoles; a reasonable value for the quadrupole moment of $H_2$ was obtained by Welsh and his collaborators (41).

For dipolar gases, $B_\varepsilon$ may be positive or negative (Ref. 36). The main factor determining the sign appears to be the shape of the molecule, i.e. the angle-dependence of the short-range intermolecular force (Ref. 42). Thus cigar-shaped polar molecules like HCN have negative $B_\varepsilon$s due to the tendency towards alignment of the type $\rightleftarrows$, while disc-shaped molecules like $CF_3H$ have positive $B_\varepsilon$s due to $\rightarrow\ \rightarrow$ alignment.

The influence of polarizability on calculated values of $B_\varepsilon$ for polar gases can be enormous (Ref. 42). It may increase $B_\varepsilon$ by an order of magnitude, implying that polarizability is probably very important in determining the permittivity of a dense polar fluid. Computer simulation studies will be required to explore this point in detail (Ref. 43).

## THE KERR EFFECT

The Kerr effect is a manifestation of the anisotropy in polarizability induced by an electrostatic field. In the case of inert gases, there is a single-atom contribution depending on the hyperpolarizability and a pair-contribution due to the partial orientation of pairs through their anisotropic interaction energy $-\frac{1}{2}\Delta\alpha_{12}\cos^2\theta F_z^2$ with the field $F_z$; θ is the angle between the inter-nuclear axis R and $F_z$ (Ref. 44). The second Kerr virial coefficient $B_K$ yields the mean-square anisotropy $\langle\Delta\alpha_{12}^2\rangle$, as does the intensity of depolarized light-scattering (Ref. 14).

For anisotropically polarizable molecules, $B_K$ is extremely difficult to calculate (Refs. 45, 46); apparently it is dependent on the short-range behaviour of the potential energy as well as the dipole and polarizability surfaces. Even the order of magnitude of $B_K$ for $CHF_3$ has not been explained.

## MAGNETIC PROPERTIES

Intermolecular forces affect the dia- and para-magnetism of molecules. Changes in the former are small, but large changes may occur in the latter when unpaired electrons overlap. Thus the reaction $2NO_2 \rightarrow N_2O_4$ clearly brings about a large reduction in the susceptibility. However, in gaseous and liquid oxygen, there is apparently only a very small difference in the potential-energy surfaces for the singlet, triplet and quintuplet states of $(O_2)_2$ (Ref. 47).

NMR spectroscopy is a useful probe of molecular interactions in gases (Refs. 48-50) and condensed phases (Refs. 51-53). Hyperfine splittings may be seen as a result of solvent interaction with a magnetic solute (Ref. 54), and hyperfine interactions in alkali-metal atoms are affected by collisions with inert-gas atoms (Ref. 55). It is clear that much can be learnt both about wavefunctions and intermolecular forces from experimental and theoretical studies of these effects.

## CONCLUSIONS

If we are to understand the effects of solute-solute and solute-solvent interactions on optical, electric, magnetic and spectroscopic properties, we shall require knowledge of both the property and the potential-energy surfaces. For polyatomic molecules, the dimensionality of these surfaces is prohibitively high, so simplifications are essential. Many-body effects may be important - they contribute minus 7 per cent of the binding energy of solid argon at absolute zero (Ref. 56), and are the sole cause of a fluctuating dipole moment (and hence of far-infrared absorption) in a monatomic liquid.

The property and potential-energy surfaces may conveniently be divided into long- and short-range parts. At long range, the molecules retain their identity and perturbation theory may be applied to relate the property of the interacting pair to those of the free molecules (Ref. 57). At short range such a description is inappropriate and we must look to ab initio computation for a quantitative understanding. A practical way forward is to curtail the long-range surface by a function of the separation which is unity for large R but which reduces its magnitude by a few percent at $R_e$ and by a larger amount at smaller values of R. Simple short-range surfaces, based on SCF computations, are then added to the modified long-range surface. Such an approach has been used for the potential energy (Refs. 58-60).

Progress in this fascinating field is likely to come through a combination of experiment and ab initio computation - the so-called supermolecule approach (Ref. 61) - providing a basis for semi-empirical energy and property surfaces (Ref. 62). Simulation may provide the best means of testing the validity of a surface and for making predictions. Much remains to be done. But the prize is rich - the ability to change molecular properties through control of the microscopic environment.

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