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Theoretical Electronic Transition Probabilities* of Heteronuclear Diatomic Molecules

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Dipole strengths of various heteronuclear diatomic molecules are calculated for high and low energy transitions of one spectral type, $^1\Sigma - {}^1\Sigma$, $\sigma - \sigma$. Through the use of increasingly accurate ground state wavefunctions it is possible to display the sensitivity of the transition probabilities to known approximations in the wavefunction. Selfconsistent field and configuration interaction effects are compared and contrasted.

Les forces d'oscilateurs dipolaires de diverses molécules diatomiques hétéronucléaires sont calculées pour les transitions de basse et haute énergie d'un type spectral $^1\Sigma - {}^1\Sigma$, $\sigma - \sigma$. Par utilisation de fonctions d'onde de l'état fondamental de plus en plus précises il est possible de montrer la sensibilité des probabilités de transition aux approximations connues sur la fonction d'onde. Les effets liés au champ S.C.F. et à l'interaction de configuration sont comparés et dlfférenciés.

Dipolstärken von zweiatomigen Molekülen mit verschiedenen Kernen wurden für Übergänge vom Typ $^1\Sigma - {}^1\Sigma$, $\sigma - \sigma$ mit großer und kleiner Energiedifferenz berechnet. In die Funktionen für den Grundzustand war eine unterschiedlich große Anzahl von Konfigurationen einbezogen worden, so daß die Abhängigkeit der Übergangswahrscheinlichkeiten vom Approximationsgrad verfolgt werden konnte. In der Diskussion wurden SCF- und CI-Effekte unterschieden.

Interest in the calculation of molecular electronic transition probabilities dates from a series of papers by R. S. Mulliken published about 28 years ago. A culminating exposition and review by Mulliken and Rieke [*1*] was published in 1941. From that date progress in achieving a more fundamental understanding of the factors involved in intensity calculations has been very slow.

First it was emphasized that several quantum mechanical operators lead to equivalent definitions of the oscillator strength for exact molecular electronic wavefunctions**.

$$f(\nabla) = \tfrac{2}{3}\,\Delta E^{-1}\,|\langle\psi_k, \nabla\,\psi_n\rangle|^2 \tag{1}$$

$$f(R) = \tfrac{2}{3}\,\Delta E\,|\langle\psi_k, R\,\psi_n\rangle|^2 \tag{2}$$

or

$$f(\nabla) = \tfrac{2}{3}\,\Delta E^{-1}\,D_M \tag{3}$$

$$f(R) = \tfrac{2}{3}\,\Delta E\,D_R \tag{4}$$

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** All units are atomic units. A third operator relation exists, but is not as useful as (1) and (2), (see Ref. [*11*]).

D_M and D_R are the dipole strengths of the transition, defined by comparison of Eqs. (1) through (4). If ψ_k and ψ_n are the exact wavefunctions of the initial and final states, then

$$f(\nabla) = f(R)\,. \tag{5}$$

Unfortunately while (5) is a *necessary* condition on the exact wavefunctions it is not *sufficient* to define them. Recently [*2*] the operator relation on which (5) is based has been examined from the point of view of perturbation theory. The resulting relation between the expectation values of ∇ and R, in each order of perturbation theory, makes it doubtful that the satisfaction of (5) may be regarded as significant evidence that the true f-value has been attained. Nor may greater significance be attached to $f(\nabla)$ or $f(R)$ until more is known about the relative rates of convergence of expectation values of ∇ and R. However one must admit that in the absence of experimental f-values or nearly exact wavefunctions, (5), or the equivalent relation from (3) and (4),

$$\Delta E = (D_M/D_R)^{1/2} \tag{6}$$

is the only available index (other than the variational energies) of the significance of the calculated dipole strengths.

Secondly, since the publication of the MULLIKEN-RIEKE review in 1941 theoreticians have involved the calculation of electronic transition probabilities in a number of derivative issues, i.e. forbidden and quasi-forbidden transitions, effects of hybridization, solvent effects, molecular crystal spectra effects, f-values for sum rules etc. All these studies show the far reaching importance of intensity calculations but are not concerned with investigation of the factors in the wavefunction which most strongly affect the dipole strength of a transition. However in the years since 1950 the increasing use of configuration interaction (CI) in molecular electronic wavefunctions established the extreme sensitivity of the dipole strength to CI. Coupled with the following detailed studies, this indicated electron correlation is an important missing ingredient in the calculation of dipole strengths from single determinental wavefunctions. SCHIFF and PEKERIS [*3*] in their exact Helium calculations have shown that $f(\nabla)$ and $f(R)$ converge to the exact oscillator strength, KELLY [*4*] has used perturbation theory on Be atom to illustrate diagrammatically the many-electron effects which contribute to the dipole strength, finally LA PAGLIA and SINANOGLU [*5*] have used the many-electron theory approach to achieve a more explicit understanding of the role of electron correlation in the transition probability. Most recently the effect of internuclear distance on the dipole strength has come under scrutiny [*6*, *7*].

The purpose of the present work is specifically aimed at observing the effect of ground state SCF and CI improvements on the dipole strength of a given transition type (${}^1\sum - {}^1\sum, \sigma - \sigma$). To outline the method of calculation LiH will be used as an example. The zero order approximation for the ground state wavefunction is the minimal basis set SCF-LCAO–MO wavefunction, with either a Slater type minimal basis set (STO) or a best minimal basis set (BM). For LiH the zero order ground state configuration is, $(1\sigma)^2\,(2\sigma)^2$. These wavefunctions were determined by RANSIL [*8*]. As part of the calculation RANSIL obtained virtual orbitals orthogonal to the occupied molecular orbitals. The virtual orbitals were later used by FRAGA and RANSIL [*9*] to improve the single determinental ground state by configuration interaction. In our notation if the transition under study is say, $2\sigma \rightarrow 3\sigma$ of LiH, then the CI ground state is written,

$$\mathrm{LiH} = c_0(1\sigma)^2\,(2\sigma)^2 + c_1(1\sigma)^2\,(3\sigma)^2 + c_2(3\sigma)^2\,(2\sigma)^2 + \ldots$$

That is, if the orbital transition is $k\sigma \rightarrow n\sigma$, then the configuration with double excitation of $k\sigma$ to $n\sigma$ is always written as the c_1 term. Of course c_0 is greater than, and usually much greater than, the other coefficients. These coefficients were chosen as the largest from the solution of the secular equation for configuration interaction.

The approximate excited state wavefunction follows from the excitation process as an orbital transition from the occupied orbital $k\sigma$ to the virtual orbital $n\sigma$, the remaining orbitals of the zero order ground state configuration are unchanged. This is a frozen-core-virtual-orbital approximation. As an example, the orbital excitation $k\sigma \rightarrow n\sigma$, yields an excited state, (core) $(k\sigma)$ $(n\sigma)$, and has a ground state, $c_0(\text{core})\,(k\sigma)^2 + c_1(\text{core})\,(n\sigma)^2 + \ldots$ The ${}^1\sum - {}^1\sum$ transition moment is then

$$\langle\psi_n, \nabla\psi_k\rangle = \frac{2}{\sqrt{2}}\{c_0\langle n\sigma, \nabla k\sigma\rangle + c_1\langle k\sigma, \nabla n\sigma\rangle + c_2\,\langle m\sigma, \nabla p\sigma\rangle + \ldots\} \tag{7}$$

and a similar expression for $\langle\psi_n, R\psi_k\rangle$. Note that the second term in Eq. (7) with the coefficient c_1 is the adjoint of the zero order matrix element.

Eq. (7) gives a complete illustration of the quantities listed in Tab. 1. For example, under LiH in Tab. 1 is the lowest energy transition, $2\sigma \rightarrow 3\sigma$, $D_M = |\langle\psi_3, \nabla\psi_2\rangle|^2$ and $D_R = |\langle\psi_3, R\,\psi_2\rangle|^2$ are calculated with the STO and BM wavefunctions and listed as shown. Each D is calculated to 3 orders of approximation, $D^{(0)}$ is D to zero order [only the c_0 term of (7)], $D^{(1)}$ is D including the entire zero order matrix element [c_0 and c_1 terms of (7)], D^T is the total D including all ground state configurations. In the next to last column is given the total number of terms which occur in (7). $(D_M/D_R)^{1/2}$ is the transition energy *if* $f(R) = f(\nabla) = f_{exakt}$, otherwise it is an index of relative changes in D_M and D_R between STO and BM wavefunctions. Alternatively the last column may be regarded as a crude estimate of the transition energy. Substitution in (3) or (4) will then yield a predicted oscillator strength. However to place this matter in some perspective we note that only one of the transitions has an assigned experimental energy, that is the lowest energy transition of the lot, $2\sigma \rightarrow 3\sigma$ LiH. Fraga and Ransil [*10*] have calculated this transition energy using the same frozen-core-virtual-orbital excited state as was used in the dipole strength calculation. They found $\Delta E = 35.9 \times \times 10^3\ \mathrm{cm}^{-1}$, compared to the experimental $\Delta E = 26.5 \times 10^3\ \mathrm{cm}^{-1}$ and the ratio $(D_M/D_R)^{1/2} = 51.7 \times 10^3\ \mathrm{cm}^{-1}$.

Discussion

Tab. 1 is the concise satement of the results of this investigation. There are displayed dipole strengths for low and high energy transitions of a variety of molecules but always for the same transition type. Furthermore the results are displayed for various approximations to the ground state wavefunction but always for the same excited state approximation. One should be able to isolate and discuss the effect of the approximations in the wavefunction and how they vary from low to high energy transitions and from molecule to molecule.

Table 1[a]

			$D^{(0)}$	$D^{(1)}$	D^{T}	No. Confgs.	$(D_M/D_R)^{1/2}$ $\times 10^{-3}\mathrm{cm}^{-1}$
			LiH $(1\sigma)^2\,(2\sigma)^2$				
$2\sigma \to 3\sigma$	STO	D_M	.0136	.0148	.0194	9	54.2
		D_R	.5160	.4770	.3172		
	BM	D_M	.0092	.0102	.0170	9	51.7
		D_R	.6084	.5454	.3054		
$2\sigma \to 4\sigma$	STO	D_M	.0312	.0390	.0374	7	139.
		D_R	.3422	.2660	.0926		
	BM	D_M	.1020	.1220	.1188	7	113.
		D_R	.8868	.7286	.4458		
$1\sigma \to 3\sigma$	STO	D_M	.0558	.0560	.0514	9	341.
		D_R	.0238	.0236	.0212		
	BM	D_M	.0964	.0970	.0904	9	386.
		D_R	.0324	.0322	.0292		
$1\sigma \to 4\sigma$	STO	D_M	.0624	.0624	.0632	8	468.
		D_R	.0128	.0128	.0138		
	BM	D_M	.2548	.2556	.2570	8	528.
		D_R	.0430	.0428	.0444		
			BH $(1\sigma)^2\,(2\sigma)^2\,(3\sigma)^2$				
$3\sigma \to 4\sigma$	STO	D_M	.2992	.3406	.3158	10	80.0
		D_R	2.4456	2.1288	2.3754		
	BM	D_M	.2826	.3172	.2890	10	82.5
		D_R	2.0108	1.7782	2.0450		
$2\sigma \to 4\sigma$	STO	D_M	.1902	.2136	.1900	9	103.
		D_R	.8226	.7274	.8609		
	BM	D_M	.1950	.2200	.1944	9	107.
		D_R	.7594	.6660	.8140		
$1\sigma \to 4\sigma$	STO	D_M	.5906	.5918	.5878	6	1423.
		D_R	.0138	.0138	.0140		
	BM	D_M	.5518	.5532	.5468	6	1463.
		D_R	.0122	.0122	.0122		
			NH $(1\sigma)^2\,(2\sigma)^2\,(\pi)^4$				
$2\sigma \to 3\sigma$	STO	D_M	.3008	.3718	.3548	9	104.
		D_R	1.9192	1.5134	1.5566		
	BM	D_M	.2602	.3270	.3112	9	108.
		D_R	1.5988	1.2350	1.2686		
$2\sigma \to 4\sigma$	STO	D_M	.0332	.0358	.0340	8	160.
		D_R	.0528	.0486	.0634		
	BM	D_M	.0968	.1034	.1000	8	203.
		D_R	.1030	.0962	.1162		

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[a] The calculation of dipole strengths from LCAO wavefunctions has for its basic step the evaluation of the integrals, $\langle a, \mathcal{O}\, b\rangle$, where a and b are atomic orbitals on centers a and b respectively. Compilations of these integrals have been published together with sample calculations and suggested procedures. See reference [2] for further details and further references.

Table 1 (continued)

			$D^{(0)}$	$D^{(1)}$	D^{T}	No. Confgs.	$(D_M/D_R)^{1/2}$ $\times 10^{-3}\text{cm}^{-1}$
NH $(1\sigma)^2\,(2\sigma)^2\,(\pi)^4$							
$1\sigma \to 3\sigma$	STO	D_M	.3610	.3610	.3590	5	2844.
		D_R	.0022	.0022	.0022		
	BM	D_M	.7122	.7131	.7085	5	2804.
		D_R	.0042	.0042	.0044		
$1\sigma \to 4\sigma$	STO	D_M	1.4330	1.4350	1.4258	5	2738.
		D_R	.0094	.0094	.0092		
	BM	D_M	1.5020	1.5040	1.4934	5	2986.
		D_R	.0082	.0082	.0080		
HF $(1\sigma)^2\,(2\sigma)^2\,(3\sigma)^2\,(\pi)^4$							
$3\rho \to 4\sigma$	STO	D_M	.5272	.6636	.6694	10	147.
		D_R	1.8062	1.3928	1.4886		
	BM	D_M	.6044	.7454	.7310	10	162.
		D_R	1.5124	1.1966	1.3292		
$2\sigma \to 4\sigma$	STO	D_M	.0026	.0028	.0052	8	145.
		D_R	.0022	.0022	.0120		
	BM	D_M	.0410	.0432	.0338	8	170.
		D_R	.0302	.0288	.0565		
$1\sigma \to 4\sigma$	STO	D_M	1.6174	1.6190	1.5686	5	4493.
		D_R	.0038	.0038	.0038		
	BM	D_M	1.7272	1.7286	1.6700	5	4832.
		D_R	.0036	.0036	.0034		
LiF $(1\sigma)^2\,(2\sigma)^2\,(3\sigma)^2\,(4\sigma)^2\,(\pi)^4$							
$4\sigma \to 5\sigma$	STO	D_M	.0042	.0046	.0052	3	132.
		D_R	.0220	.0214	.0142		
$4\sigma \to 6\sigma$	STO	D_M	.1700	.1766	.1708	6	928.
		D_R	.0460	.0444	.0098		
$3\sigma \to 5\sigma$	STO	D_M	.0002	.0002	.0002	3	67.
		D_R	.0028	.0028	.0028		
$2\sigma \to 5\sigma$	STO	D_M	.0344	.0346	.0346	3	329.
		D_R	.0154	.0152	.0154		
$1\sigma \to 5\sigma$	STO	D_M	.0156	.0156	.0156	1	—
		D_R	.0000	.0000	.0000		
BF $(1\sigma)^2\,(2\sigma)^2\,(3\sigma)^2\,(4\sigma)^2\,(5\sigma)^2\,(\pi)^2$							
$5\sigma \to 6\sigma$	STO	D_M	.2936	.3188	.2964	5	100.
		D_R	1.5010	1.3778	1.4172		
$4\sigma \to 6\sigma$	STO	D_M	.3744	.3974	.3784	5	226.
		D_R	.3236	.3042	.3554		
$3\sigma \to 6\sigma$	STO	D_M	.0734	.0764	.0622	5	247.
		D_R	.0350	.0336	.0490		
$2\sigma \to 6\sigma$	STO	D_M	.5358	.5368	.5266	4	1453.
		D_R	.0118	.0118	.0120		
$1\sigma \to 6\sigma$	STO	D_M	.8818	.8818	.8954	3	4412.
		D_R	.0022	.0022	.0022		

Table 1 (continued)

			$D^{(0)}$	$D^{(1)}$	D^{T}	No. Confgs.	$(D_M/D_R)^{1/2}$ $\times 10^{-3}$cm^{-1}
			CO $(1\sigma)^2\,(2\sigma)^2\,(3\sigma)^2\,(4\sigma)^2\,(5\sigma)^2\,(\pi)^4$				
$5\sigma \rightarrow 6\sigma$	STO	D_M	.6912	.7408	.6948	5	173.
		D_R	1.1650	1.0846	1.1176		
$4\sigma \rightarrow 6\sigma$	STO	D_M	.6798	.7040	.6694	4	389.
		D_R	.2014	.1944	.2126		
$3\sigma \rightarrow 6\sigma$	STO	D_M	.3526	.3708	.3274	4	310.
		D_R	.1430	.1358	.1640		
$2\sigma \rightarrow 6\sigma$	STO	D_M	.9360	.9380	.9360	3	2285.
		D_R	.0084	.0084	.0086		
$1\sigma \rightarrow 6\sigma$	STO	D_M	1.282	1.284	1.284	2	3790.
		D_R	.0044	.0044	.0044		

1. The BM dipole strengths often vary appreciably from the STO dipole strengths. Note that when they do so differ, they differ in each order of approximation from the single configuration to the multiconfiguration ground state. That is, the correction due to ζ variation is included even in the single configuration dipole strength. This is typical for an SCF effect unrelated to electron correlation, which is as it should be for ζ variation. Of course the effect is most marked where the BM ζ values differ most from the STO values. As an example the BM and STO results for LiH are very different as are the ζ values, (2.70, 0.65 and 0.65 STO versus 2.69, 0.70 and 0.84 BM). While the BM and STO results for BH are only slightly different as are the ζ values, (4.7, 1.3 and 1.3 STO versus 4.68, 1.29 and 1.31 BM).

2. In general STO and BM wavefunctions give $(D_M/D_R)^{1/2}$ of qualitative and most often quantitative similarity. This was an unexpected result of the comparative calculations. Even when STO and BM dipole strengths differ by a factor of 2, as in $1\sigma \rightarrow 3\sigma$ of NH, comparable transition energies were obtained. This may mean that the SCF differences which distinguish BM from STO wavefunctions affect the matrix elements of ∇ and R in a proportionate manner. However the BM dipole strengths are clearly superior since they always give the correct order of transition energies in a given molecule, while in several cases the STO dipole strengths invert the order of certain transitions, i.e. NH, HF etc.

3. As for the effect of configuration interaction one first notes the lack of sensitivity to CI of the high energy transitions. This may not imply that these transitions have dipole strengths that are accurately determined in zero order but rather that CI is very slowly convergent for electron correlation effects in the inner shells. That is, if ψ_n in (7) is a wavefunction with an inner shell excitation then c_1 and the other coefficients (which are related to correlation in the inner shell [5]) are all very small. The efficacious way of including inner shell electron correlation is by placing the correlation factor r_{12} directly into the wavefunction.

4. Finally we note a marked difference between the $D^{(0)}$ and $D^{(1)}$ dipole strength approximation for most of the low energy transitions. As stated previously this

Table 2

		$(D_M^{(0)}/D_R^{(0)})^{1/2}$	$(D_M^{(1)}/D_R^{(1)})^{1/2}$	$(D_M^T/D_R^T)^{1/2} \times 10^{-3}$ cm^{-1}
BH $3\sigma \to 4\sigma$	STO	76.8	87.8	80.0
	BM	82.3	92.7	82.5
NH $2\sigma \to 3\sigma$	STO	86.9	108	104
	BM	88.5	113	108

difference is entirely due to inclusion of the one configuration, (core) $(n\sigma)^2$, into the ground state when the excitation is, (core) $(k\sigma)^2 \to$ (core) $(k\sigma)$ $(n\sigma)$. Unlike the BM and STO differences the effect of CI can often be far from proportionate for ∇ and R dipole strengths. The c_1 term in (7) which distinguishes $D^{(0)}$ from $D^{(1)}$ must always have a different sign for ∇ and R from the c_0 matrix elements for these operators. This is because R is a hermitian operator while ∇ is anti-hermitian. Consider the transition $3\sigma \to 4\sigma$ of BH, Tab. 2 shows that the change induced in the dipole strength ratio by the introduction of just the doubly excited configuration c_1(core) $(4\sigma)^2$ into the ground state is twice as great as the change between STO and BM dipole strength ratios. Again for the lowest energy transition of NH (Tab. 2) we see a pronounced CI effect far more important than the SCF changes.

Conclusions

In the present work we have examined the dipole strengths of one type of transition in one type of molecule with various approximations to the ground state wavefunctions. The differences between BM and STO wavefunctions are SCF (orbital size and shape) effects reflected in small changes in the LCAO coefficients and the atomic ζ values. These changes seem to have roughly proportionate effects on ∇ and R dipole strengths as measured by the ratio $(D_M/D_R)^{1/2}$. This is in agreement with the work [*11*] of Phillipson and Ehrenson who plotted the integrands of transition moment integrals of ∇ and R for a H-atom transition and found comparable radial dependences. The effect of CI was found to be strongest for the lowest energy transition. One is led to be rather wary of Hartree-Fock or SCF dipole strengths especially for the low energy transitions.

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