VARIATIONAL UPPER AND LOWER BOUNDS TO DIPOLE TRANSITION MOMENTS*

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Electric-dipole transition moments are calculated by a variational procedure which gives rigorous upper and lower bounds even though the exact wave functions are unknown. The method is applied to the lowest optical transition ($1s\sigma \rightarrow 2p\sigma$) of the hydrogen molecule ion, with satisfactory results.

In this Letter we describe a method which gives rigorous upper and lower limits to transition moments

$$w_{ab} = \langle \Psi_a | W | \Psi_b \rangle, \tag{1}$$

even when neither of the true wave functions Ψ_a, Ψ_b is known exactly. The upper and lower bounds may be variationally strengthened to any desired degree. We deal here with the important special case of radiative processes in which the electric dipole mechanism dominates; then, in the length formulation,[1] W is a component of the total electronic dipole-moment operator connecting electronic states Ψ_a and Ψ_b of different symmetry.

In the conventional approach,[2] approximations Φ_a and Φ_b are developed separately for each of the two states, usually by an energy-minimum criterion, and the transition moment is estimated as

$$\tilde{w}_{ab} = \langle \Phi_a | W | \Phi_b \rangle. \tag{2}$$

However, important contributions to the integral (1) may arise from regions of configuration space which do not appreciably affect the energy of either state.[3] The approximation (2) is then highly sensitive to rather small details (including the correlation effects[4]) of the two wave functions, and the sign of the error is unknown. Some special variational principles have been suggested, but these may be only stationary (i.e., saddle-point, rather than maximum or minimum) principles,[5] or only semirigorous,[6] or may require exact knowledge of one or the other true wave function,[7] or may bound the answer on one side only,[8] etc. These and other limitations are avoided in the present approach.

Our development is based on the inequalities[9]

$$\langle \chi | F | \Psi \rangle \leq S\langle \chi | F | \Phi \rangle + \epsilon[\langle \chi | F^2 | \chi \rangle - \langle \chi | F | \Phi \rangle^2]^{1/2}, \tag{3a}$$

$$\langle \chi | F | \Psi \rangle \geq S\langle \chi | F | \Phi \rangle - \epsilon[\langle \chi | F^2 | \chi \rangle - \langle \chi | F | \Phi \rangle^2]^{1/2}, \tag{3b}$$

where S is the (positive) overlap integral of the normalized functions Φ and Ψ,

$$S \equiv \langle \Phi | \Psi \rangle,$$

and

$$\epsilon \equiv (1-S^2)^{1/2},$$

and where F is an arbitrary Hermitian operator, with all matrix elements assumed real. Inequalities (3) are first applied to the transition moment (1), with $\chi = \Psi_a$, $\Psi = \Psi_b$, $\Phi = \Phi_b$, to give

$$w_{ab} \leq S_b \langle \Psi_a | W | \Phi_b \rangle + \epsilon_b [\langle \Psi_a | W^2 | \Psi_a \rangle - \langle \Psi_a | W | \Phi_b \rangle^2]^{1/2},$$

$$w_{ab} \geq S_b \langle \Psi_a | W | \Phi_b \rangle - \epsilon_b [\langle \Psi_a | W^2 | \Psi_a \rangle - \langle \Psi_a | W | \Phi_b \rangle^2]^{1/2}.$$

A second application of (3) to $\langle \Psi_a | W | \Phi_b \rangle$ (with $\chi = \Phi_b$, $\Psi = \Psi_a$, $\Phi = \Phi_a$) then yields

$$w_{ab} \leq S_a S_b \tilde{w}_{ab} + \epsilon_a S_b \Delta_{ab} + \epsilon_b \{\langle \Psi_a | W^2 | \Psi_a \rangle - [S_a \tilde{w}_{ab} - \epsilon_a \Delta_{ab}]^2\}^{1/2}, \tag{4a}$$

$$w_{ab} \geq S_a S_b \tilde{w}_{ab} - \epsilon_a S_b \Delta_{ab} - \epsilon_b \{\langle \Psi_a | W^2 | \Psi_a \rangle - [S_a \tilde{w}_{ab} - \epsilon_a \Delta_{ab}]^2\}^{1/2}, \tag{4b}$$

where

$$S_a \equiv \langle \Phi_a | \Psi_a \rangle, \quad S_b \equiv \langle \Phi_b | \Psi_b \rangle, \quad \epsilon_a \equiv (1-S_a^2)^{1/2}, \quad \epsilon_b \equiv (1-S_b^2)^{1/2}, \quad \Delta_{ab} \equiv (\langle \Phi_b | W^2 | \Phi_b \rangle - \tilde{w}_{ab}^2)^{1/2}.$$

Both $\tilde{w}_{ab}$ and Δ_{ab} are calculated directly, but S_a, S_b, and $\langle \Psi_a | W^2 | \Psi_a \rangle$ must be replaced by appropriate bounds. With the notation S_{a+} and S_{a-}, respectively, for the upper and lower bounds to S_a, etc., the

proper choices are found to be

$$w_{ab} \leq S_{a+} S_{b+} \tilde{w}_{ab} + \epsilon_{a+} S_{b+} \Delta_{ab} + \epsilon_{b+} \{ \langle \Psi_a | W^2 | \Psi_a \rangle_+ - [S_{a-} \tilde{w}_{ab} - \epsilon_{a+} \Delta_{ab}]^2 \}^{1/2}, \quad (5a)$$

$$w_{ab} \geq S_{a-} S_{b-} \tilde{w}_{ab} - \epsilon_{a+} S_{b-} \Delta_{ab} - \epsilon_{b+} \{ \langle \Psi_a | W^2 | \Psi_a \rangle_+ - [S_{a-} \tilde{w}_{ab} - \epsilon_{a+} \Delta_{ab}]^2 \}^{1/2}. \quad (5b)$$

[Here it is assumed that the coordinate system is chosen to make $\tilde{w}_{ab}$ positive, and that S_{a-} is sufficiently near unity to satisfy

$$(1-S_{a-}^2)^{1/2}/S_{a-} \leq \tilde{w}_{ab}/\Delta_{ab}.]$$

The problem is thus reduced to the evaluation of an upper bound for $\langle \Psi_a | W^2 | \Psi_a \rangle$ and upper and lower bounds for the overlap integrals S_a and S_b.

Rebane and Braun[8] have recently provided a useful upper bound to the expectation value $\langle \Psi_a | W^2 | \Psi_a \rangle$ in an N-electron system,

$$\langle \Psi_a | W^2 | \Psi_a \rangle \leq N/2(E_b - E_a) \text{ a.u.}, \quad (6)$$

which is valid when Ψ_b is the lowest state of its symmetry type. Other upper bounds might also be considered,[10] but high accuracy is not so critical for this particular element.

For the overlap integrals S_a and S_b, various formulas for upper and lower bounds have become available,[11,12] both for ground and excited states. If one makes the particularly simple choice of Eckart's criterion[13,11] for S_{a-} and S_{b-}, the lower member of (5b) can be shown to reduce back to the strongest form of the lower bound obtained by Rebane and Braun.[8] For applications to the ground state of a given symmetry, the Eckart criterion will indeed be the practical choice in many cases, but formulas (5a) and (5b) allow a considerable extension both for ground and excited states, and give also a corresponding upper bound to the transition moment.

An elementary numerical application of (5a) and (5b) has been made, following Rebane and Braun,[8] to the lowest optical transition ($1s\sigma \rightarrow 2p\sigma$) in the hydrogen molecular ion, H_2^+. The two states were approximated as simple symmetric or antisymmetric linear combinations of screened $1s$ atomic orbitals on the two nuclear centers,[14]

$$\Phi_{1s\sigma} \approx \exp(-\alpha r_A) + \exp(-\alpha r_B),$$

$$\Phi_{2p\sigma} \approx \exp(-\beta r_A) - \exp(-\beta r_B),$$

with orbital exponents α and β as adjustable parameters. The Eckart criterion and Eq. (6) were employed,[15] together with the simplest possible upper limit to overlap, $S_{1+} = S_{2+} = 1$. Both the upper and the lower bounds were optimized with respect to α and β at each internuclear separation R.

Figure 1 shows the calculated upper and lower bounds to the molecular transition moment over a range of R, and compares these with the accurate values obtained by Bates.[16] Also shown is the ordinary variational estimate [i.e., Eq. (2), with α and β determined from the energy-minimum criterion], which virtually coincides, to

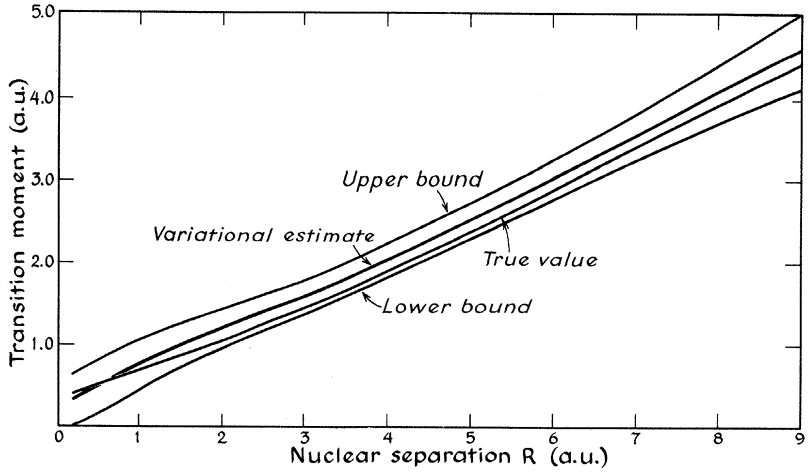

FIG. 1. Rigorous upper and lower bounds for $1s\sigma \rightarrow 2p\sigma$ transition moment in H_2^+, $0.2 \leq R \leq 9.0$ a.u., as calculated in the linear combination of atomic orbitals approximation from the formulas of the text. The accurate values (Ref. 16) as well as the ordinary variational estimate are shown for comparison. Values were computed at the points given by Bates and connected by a smooth curve.

the accuracy plotted, with the mean of the upper and lower bounds. The true value is seen to fall quite near the rigorous bound over a considerable range of R, and one may conclude that the error bounds are of satisfactory quality in view of the approximate functions employed. The guaranteed accuracy of the mean of the upper and lower bounds is somewhat better than 10% in the range $R \approx 4$-9 a.u., and though the relative accuracy falls off as the transition moment diminishes, the magnitude of the possible error remains roughly constant even quite near the united-atom limit. Improved variational descriptions of either state would, of course, further tighten the error bounds, as would a more careful treatment of the overlap integrals S_a, S_b even in the linear combination of atomic orbitals approximation.

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ELASTIC SCATTERING OF LOW-ENERGY PROTONS BY HELIUM

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Elastic differential scattering experiments have been performed on the system p + He at collision energies low enough to exclude inelastic channels. The experimental cross section is compared with the results of JWKB partial-wave calculations in which *ab initio* calculations of the interatomic potential have been employed. This comparison is seen to provide a very sensitive test of the accuracy of such potentials.

The relative differential cross section for the elastic scattering of low-energy protons by helium atoms has been measured and is believed to provide the first direct experimental verification of ab initio calculations for the ground-state intermolecular potential of the HeH^+ molecular ion. The incentive for such low-energy investigations of the proton-helium system rests upon several basic considerations. First, the proton-helium system is one of only a few systems for which ab initio calculations for several molecular states are available and therefore can serve as a basis for detailed scattering calculations. Also if the scattering experiment is performed