Guest–Host Interactions: An Examination of the Solvent-Induced Spectral Shift in a Model System

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In this paper we study the effect of a surrounding lattice of He atoms on the manifold of electronic states of the H_2^+ molecule-ion. One-center expansions of the molecular wavefunctions are employed, calculated by the Tibbs–Wannier method. The spherically averaged wavefunctions are in good agreement with the known exact solutions.

A detailed study of the environmental effect of the He lattice leads to the prediction of a blue shift of the first electronic transition, arising from a delicate balance between changes in the impurity excitation energy, Coulomb, exchange, van der Waals, and three-center interaction terms. The signs of the various energy changes are rationalized in terms of the overlap charge density. These results are compared with previous treatments of environmental spectral shifts based on continuum models.

I. INTRODUCTION

IT is commonly observed that the frequency of a molecular electronic transition shifts when a molecule is transferred from the dilute gas to a solution in a condensed state of matter. This electronic frequency shift may be considered to measure the difference between the interaction energy of the absorber and the surrounding medium when it is in its excited state and in its ground state. Indeed, it is commonly assumed that the interactions in the ground state and excited state can be represented in terms of a pairwise additive intermolecular potential which is different for each state. The total change in interaction energy is then obtained from the difference in the intermolecular pair potentials and the density of surrounding molecules, presumed to be known as a function of distance from the absorbing center. By consideration of the time constants characteristic of various molecular motions, it is easily established that electronic transitions occur in an essentially static environment, whereupon the distribution of molecules which is important is that characteristic of the ground state assembly. For the particular case of a nonpolar absorber in a nonpolar solvent,[1] the application of the multipole expansion to evaluate the interaction energy leads to a relationship of the form

$$\nu^0-\nu \propto f(n^2-1)/(2n^2+1),$$

where ν and ν^0 are the absorption frequencies in solution and vacuum, f is the oscillator strength of the transition, and n is the refractive index of the solvent. This relation, which is valid only for nonoverlapping charge distributions, predicts that the transition frequency is always red-shifted on passage from the gas phase to a condensed phase. Examples of such behavior are to be found in the $\pi\rightarrow\pi^*$ transitions of planar aromatic compounds.

It is also possible to discuss the effects of specific molecular interactions on the absorption spectrum. The most important of the specific interactions are hydrogen bonding and charge transfer. For the simple system we wish to discuss herein the possibility of hydrogen bonding does not exist, and we shall examine the role of charge transfer states in another paper.[2] Suffice it to say that these states are unimportant for the system studied herein but are of great importance in a large number of other systems.

A common feature of the theoretical treatments which lead to a representation of the interaction in terms of the multipole expansion is the assumption that the charge density of the absorbing molecule does not overlap with that of the surrounding host molecules. The simplest of the treatments then parameterize the effects of the host in terms of one or a few macroscopic constants (such as the refractive index). Although the Longuet-Higgins–Pople theory[1] does not reduce the description to that level, the role of the solvent is restricted to be that of a reservoir for dispersion forces. When the overlap between solute and solvent molecular wavefunctions is small, these theories work rather well, as noted above. However, there are large classes of electronic transitions for which the assumption of vanishing overlap is incorrect. In these cases there are several major factors which influence the manifold of energy levels of the solute molecule. The resultant spectrum then represents only the end product of a delicate balance between many competing changes, and in order to understand the nature of solvent effects it is necessary to systematically construct an analysis in which each of the competing changes is separately discussed. At first sight, it would appear that no simple parameterization in terms of the macroscopic properties of the solvent will result in an adequate representation of the system. We discuss this remark more fully after detailing the analysis of a simple model system.

In order to elucidate the delicate balance alluded to above, it is obviously desirable to study a model system for which calculations can be performed with high

[1] H. C. Longuet-Higgins and J. A. Pople, J. Chem. Phys. **27**, 192 (1957).

[2] S. Webber, S. A. Rice, and J. Jortner, J. Chem. Phys. **41**, 2911 (1964).

accuracy. Independently of the work reported herein, Keil and Gold[3] have studied the excitation energies for the $1s$–$2p$ and $1s$–$2s$ transitions of a hydrogen atom present as a substitutional impurity in solid argon. Their results are discussed in Sec. VI. With a somewhat different goal in mind, we independently chose to study the hypothetical solid solution in which an H_2^+ molecule ion is at a substitutional site in a solid He lattice. In choosing this system we sought to minimize the artifacts which may arise when inaccurate wavefunctions are used. The molecule ion H_2^+ was chosen for the solute, rather than the hydrogen atom, because we also intended to examine the usefulness of one-center expansion procedures in describing the upper excited states of diatomic molecules. Using the results of the one-center expansion as a starting point, later papers from this laboratory will report experimental and theoretical studies of the spectra of diatomic molecules present as solutes in very simple solids. Our interests are focused on the nature of the lowest excited states in the mixed solid, on the changes induced in the Rydberg states by the surrounding medium, and on the mechanism of the process of photoionization. It should be noted that even the simple system studied herein is complex enough to illustrate all the facets of the theoretical analysis. It is found that:

(a) The predicted blue shift of the transition energy arises from a delicate balance between changes in the impurity excitation energy, the Coulomb and exchange energies, the van der Waals energy, etc.

(b) The signs of the various energy changes are easily rationalized in terms of the effects of the overlap charge density but there appears no direct correspondence between this work and the cavity continuum model.[4]

(c) Because of the delicate balance between the several changes which lead, only as a final result, to the shift in transition energy, it appears unlikely that any simple parameterization using macroscopic properties of the host medium can lead to a quantitative description of the effects of the host medium on impurity transitions.

II. DEFINITION OF THE MODEL SYSTEM

The goal of the analysis reported herein is to contribute to the understanding of the origin of spectral shifts in mixed solids. Since we are not, at present, interested in reproducing or explaining the results of particular experiments, it is convenient to simplify the analysis by discarding accidental properties of the H_2^+:He system which are irrelevant to our goal. The model system we choose to study is defined by the following:

(1) The interaction between the charge of the H_2^+ and the surrounding medium is disregarded. Although in the real system H_2^+:He, the polarization of the lattice would be an important effect, we choose to regard the H_2^+ as a *prototype neutral solute*, selected only because the available wavefunctions are accurate.

(2) As a preliminary to work now in progress, we treat H_2^+ as a spherically symmetric solute. Again, the H_2^+ is considered to be a *prototype* spherically symmetric solute, chosen because accurate wavefunctions may be obtained. In addition, the one-center expansion procedure used forms the first stage of a more general theory of the properties of diatomic solutes in simple solids.

(3) As a corollary of (2), the orientation of H_2^+ with respect to the surrounding medium need not be considered.

(4) The H_2^+ is assumed to occupy a substitutional position in the He lattice, with no change in lattice parameter (i.e., no relaxation of the lattice about the guest molecule).

Assumptions (1)–(4) clearly distinguish the model system considered herein from the real system H_2^+:He.

III. HYDROGEN MOLECULE-ION WAVEFUNCTION

The hydrogen molecule-ion has been studied many times and is one of the very few systems for which an exact solution to the Schrödinger equation can be obtained. Now, it is possible to represent the wavefunctions of H_2^+ in a one-center expansion with high accuracy. This representation is particularly valuable for problems of the type considered herein. In a one-center expansion, the potential energy of the nuclear frame is expanded in spherical harmonics about some center. Of course, the convergence of the spherical harmonic expansion depends on the nuclear geometry. For the case $V(\theta)=V(\pi-\theta)$ all spherical harmonics antisymmetric in $\cos\theta$ vanish, while for highly excited states it may be anticipated that high order terms in the spherical harmonic expansion will be small, and the behavior dominated by the leading term, which has spherical symmetry. When the potential of the nuclei of the H_2^+ molecule-ion is expanded as described, and only the leading term retained, it is found that

$$V=-2e^2/r_0; \qquad r\leq r_0,$$
$$V=-2e^2/r; \qquad r>r_0, \tag{1}$$

where r_0 is one-half the internuclear separation. The potential defined by Eq. (1) was first studied by Tibbs,[5] and then in great detail by Wannier,[6] and it has been used by Chen[7] to describe the ground state and several excited s states of H_2^+. By comparison with the exact electronic energies, it is found that in the ground state the one-center expansion is in error by only 4%, and in the $2s$ ($2s\sigma$) and $3s$ ($3s\sigma$) states the error in energy drops to 3% and 2%, respectively. Moreover, the

[3] T. Keil and A. Gold, Phys. Rev. **136**, A252 (1964).
[4] J. Jortner and C. A. Coulson, Mol. Phys. **4**, 451 (1961).
[5] S. R. Tibbs, Trans. Faraday Soc. **35**, 1471 (1939).
[6] G. H. Wannier, Phys. Rev. **64**, 359 (1943).
[7] T. C. Chen, J. Chem. Phys. **29**, 347 (1958).

TABLE I. Wavefunctions of H_2^+ with Tibbs-Wannier potential and their Slater fitting.

1s				2p			
r	ψ	Slater fitting	$\psi_s-\psi$	r	$r^{-1}F(r)$	Slater fitting	$\phi_s-\phi$
0	0.32143	0.42559	+0.10416	0.11455	0.05602	0.06238	−0.00636
0.1	0.32048	0.31785	−0.00263	0.34364	0.16274	0.15552	+0.00722
0.2	0.31761	0.29201	−0.02560	0.57273	0.25409	0.25479	−0.00070
0.3	0.31285	0.29439	−0.01846	0.80182	0.32177	0.31695	−0.00482
0.4	0.30626	0.30134	−0.00492	1	0.35674	0.35763	−0.00089
0.5	0.29788	0.30384	+0.00596	1.21000	0.36830	0.36861	−0.00031
0.6	0.28775	0.29952	+0.01177	1.44	0.36175	0.36143	+0.00032
0.7	0.27592	0.28897	+0.01305	1.69	0.34086	0.33967	+0.00110
0.8	0.26240	0.27369	+0.01129	1.96	0.30965	0.30771	+0.00194
0.9	0.24721	0.25533	+0.00812	2.25	0.27211	0.26980	+0.00231
1.0	0.23028	0.23528	+0.00500	2.56	0.23185	0.22962	+0.00223
1.1	0.21182	0.21468	+0.00286	2.89	0.19187	0.19009	+0.00178
1.2	0.19292	0.19436	+0.00144	3.24	0.1543	0.15331	+0.00112
1.3	0.17439	0.17482	+0.00043	3.61	0.12101	0.12050	+0.00051
1.4	0.15675	0.15644	−0.00031	4.0	0.09239	0.09244	−0.00005
1.5	0.14025	0.13939	−0.00086	4.41	0.06881	0.06923	−0.00042
1.7	0.11113	0.10962	−0.00151	4.84	0.05004	0.05065	−0.00061
2.0	0.07697	0.07518	−0.00179	5.29	0.03562	0.03622	−0.00060
2.5	0.04050	0.03915	−0.00135	5.76	0.02503	0.02532	−0.00029
3.0	0.02082	0.02013	−0.00069	6.25	0.10777	0.01730	+0.00047
3.5	0.01056	0.01027	−0.00029	6.76	0.01334	0.01157	+0.00177
				7.29	0.01077	0.00757	+0.00320
				7.84	0.00714	0.00485	+0.00229

shapes of the potential energy curves, especially for the $2s\sigma$ and $3s\sigma$ molecular states, are in excellent agreement with the computed curves for the model $2s$ and $3s$ states.[7] Finally, it should be pointed out that if an angularly dependent potential is added to Eq. (1), say $V_p(r, \theta, \phi)$, then all matrix elements of this potential between spherically symmetric states vanish. Since the angular potential cannot connect the spherically symmetric states defined by Eq. (1), the eigenfunctions of the Tibbs–Wannier potential represent the limit of approximating the one-electron molecular wavefunctions by an exhaustive set of spherically symmetric functions.

For our purposes it was necessary to extend the published calculations and obtain the eigenfunctions and eigenvalues of H_2^+, in the one-center scheme, for a number of hitherto unstudied states. Wannier has given an analytic solution of the Schrödinger equation for the case that the potential is given by Eq. (1). However, the expressions given are cumbersome and the utility of the solution is limited because its form necessitates undertaking a complete recomputation for every value of the effective principal quantum number. Wannier's solution is expressed in terms of the Whittaker function, $W_{k,l+\frac{1}{2}}(z)$, for which there exists[8] a convenient series expansion in powers of k^{-2}, with coefficients given in terms of Bessel functions. Once these coefficients are known for a given value of l, the function $W_{k,l+\frac{1}{2}}(z)$ is easily computed for any value of k. The connection between the Whittaker function and properties of the molecule is made by noting that k is the effective principal quantum number and l is the azimuthal quantum number.

The wavefunction of the H_2^+ molecule-ion is expressible in the form

$$\psi_1=(1/r)F_1(r)Y_{lm}(\theta,\phi); \qquad r<r_0, \tag{2}$$

$$\psi_2=(1/r)F_2(r)Y_{lm}(\theta,\phi); \qquad r>r_0, \tag{3}$$

with Y_{lm} the spherical harmonic of order l, m and

$$F_1(r)=xJ_{l+\frac{1}{2}}\{(x/2x_0)[1-(x_0/16k^2)]^{\frac{1}{2}}\}, \tag{4}$$

$$F_2(r)=W_{k,l+\frac{1}{2}}(z)$$
$$=k^{-l-1}\Gamma(k+l+1)[\cos(k-l-1)\textstyle\prod {}^0U^{(l,k)}(x)$$
$$+\sin(k-l-1)\textstyle\prod {}^1U^{(l,k)}(x)] \tag{5}$$

and

$$x=4r^{\frac{1}{2}}=2(kz)^{\frac{1}{2}}, \tag{6}$$

$$U^{(l,k)}(x)=\sum_{n=0}^{\infty}k^{-2n}U_n^{(l)}(x), \tag{7}$$

$$U_n^{(l)}(x)=\tfrac{1}{2}xV_n^l(x). \tag{8}$$

Of the remaining undefined symbols, $V_n^l(x)$ is a function of the zeroth and first cylinder functions, C_0, C_1, and ${}^0U^{(l,k)}(x)$ and ${}^1U^{(l,k)}(x)$ in Eq. (5) differ from $U^{(l,k)}(x)$ only in that the cylinder functions $C_m(x)$ are replaced by $J_m(x)$ and $Y_m(x)$, respectively, in $V_n^l(x)$.

The convergence of the series expansion of the $U^{(l,k)}(x)$ is, in general, very rapid. However, for the ground state of H_2^+ the convergence is too slow to be useful. For this case the exact ground state wavefunction[9] was transformed using a representation in spherical coordinates centered at the midpoint of the internuclear axis. The resultant wavefunction was averaged over angles. Finally, for convenience, all the normalized wavefunctions used herein were fitted to a linear combination of Slater orbitals. The computed wavefunctions are tabulated in Table I, and the Slater orbital fits are

[8] T. S. Kuhn, Quart. Appl. Math. **9**, 1 (1951).

[9] D. R. Bates, K. Ledsham, and A. L. Stewart, Trans. Roy. Soc. (London) **A246**, 215 (1953).

(the functions $\chi(n, l, \zeta)$ are Slater functions)

$$\psi_{1s}=0.091656\chi(1s, 6.25342)+1.31544\chi(1s, 1.35091)-0.49700\chi(1s, 3.1241),$$

$$\epsilon_{1s}=-1.102625 \text{ a.u.}, \quad (9)$$

$$\psi_{2p}=1.00736\chi(2p, 0.94304)+0.0041281\chi(2p, 8.34976-0.041881\chi(2p, 3.46374),$$

$$\epsilon_{2p}=-0.47522 \text{ a.u.} \quad (10)$$

A comparison of the averaged wavefunction described above for the ground state, and the spherical wavefunction computed by Cohen and Coulson[10] shows them to be numerically identical.

The energies displayed in Eqs. (9) and (10) are computed at the equilibrium internuclear distance, $r_0=1$.

IV. CALCULATION OF THE EXCITATION ENERGY[11]

We now turn to the calculation of the excitation energy of the solute H_2^+ at a substitutional site in a lattice of He atoms. An examination of the energy level diagrams of He and H_2^+ shows that it is safe to assume that the first excited state of H_2^+ does not mix with states of the He.

In somewhat more detail, we note that the separation between the first excited states of H_2^+ and He is 4 eV. For appreciable mixing to occur (i.e., for the energy to be changed by 0.1 eV) the matrix element connecting these states must be 0.7 eV. It is found that the required matrix elements are not this large, and therefore configuration interaction between solute and solvent can be neglected in this model system.

The effects of configuration mixing were calculated using the supermolecule formalism. An H_2^+ molecule ion and its near neighbors are considered to form a "supermolecule" for which properly symmetrized molecular orbitals are constructed.[12] A configuration interaction calculation of the mixing of the first excited host state and the central particle excited state is then performed. Since the formalism is essentially identical with that used by Webber, Rice, and Jortner,[2] and since the results indicate that the mixing is very small, we shall not reproduce the formulas or details herein. Suffice it to say that direct calculation of the matrix element connecting the first excited host state to the first excited guest state leads to a value of 0.1 eV. By a direct application of perturbation theory, we then conclude that the inclusion of guest–host state mixing alters our calculations by only 0.0025 eV, and can therefore be neglected.

In the following we shall also assume that the Born–Oppenheimer approximation has been made (and is valid) so that only electrostatic interactions need be discussed. The wavefunctions for the system may now be constructed in the form of a product over all atoms in the crystal and the substitional impurity, i.e.,

$$\Psi_0=\mathcal{A}\psi_{Aa}\prod_I\prod_{i\neq a}\psi_{Ii}, \quad (11)$$

$$\Psi_0=\mathcal{A}\bar{\psi}_{Aa}\prod_I\prod_{i\neq a}\bar{\psi}_{Ii}, \quad (12)$$

where $\mathcal{A}$ is the antisymmetrization operator, I refers to a nucleus located at a lattice site, i refers to an electron, and the symbols Aa are reserved for the impurity, ath electron. It is the electron on the impurity center which will make the transition under consideration. In Eqs. (11) and (12),

$$\bar{\psi}_{Ii}=\psi_{Ii}=\phi_{Ii}, \quad (13)$$

$$\psi_{Aa}=(\phi_{Aa}-\sum_{Ii}S_{Aa,Ii}\phi_{Ii})(1-\sum_{Ii}S^2_{Aa,Ii})^{-\frac{1}{2}}, \quad (14)$$

$$\bar{\psi}_{Aa}=(\bar{\phi}_{Aa}-\sum_{Ii}S'_{Aa,Ii}\phi_{Ii})(1-\sum_{Ii}S'^2_{Aa,Ii})^{-\frac{1}{2}}, \quad (15)$$

and the ϕ_{Ii}, ϕ_{Aa} are solutions of the Hartree–Fock equations for atom I and the impurity, respectively. As usual $S_{Aa,Ii}=\langle\phi_{Aa}\mid\phi_{Ii}\rangle-\delta_{AI}\delta_{ai}$ is the overlap integral between the states characterized by the functions ϕ_{Aa}, ϕ_{Ii} and $S'_{Aa,Ii}=\langle\bar{\phi}_{Aa}\mid\phi_{Ii}\rangle-\delta_{AI}\delta_{ai}$. The overbar is used in Eqs. (12), (13), and (15) to indicate an excited state. The content of Eq. (13) is equivalent to the statement that the impurity center, in both its ground and excited states, interacts with a lattice of atoms all of which are in their ground state.

Using standard methods it may be shown that the excitation energy of the impurity has the form

$$\Delta E=E_{at}+E_c+E_x+E_T+\Delta E_{VdW} \quad (16)$$

with[13]

$$E_{at}=\frac{1}{N'}\bar{E}_{Aa}-\frac{1}{N'}\sum_{I\neq A}\sum_i S'_{Aa,Ii}E_{Ii}-\frac{1}{N}E_{Aa}+\frac{1}{N}\sum_{I\neq A}\sum_i S^2_{Aa,Ii}E_{Ii}, \quad (17)$$

$$E_c=(1/N')[\langle\overline{Aa}\mid\sum_{J\neq A}z_J\mid\overline{Aa}\rangle+\sum_{Ii\neq Aa}J(\overline{Aa}, Ii)+\sum_{Ii\neq Aa}S'^2_{Aa,Ii}\langle Ii\mid\sum_{J\neq I}z_J\mid Ii\rangle+\sum_{Kk\neq Ii\neq Aa}S'^2_{Aa,Kk}J(Kk, Ii)]$$
$$-(1/N)[\langle Aa\mid\sum_{J\neq A}z_J\mid Aa\rangle+\sum_{Ii\neq Aa}J(Aa, Ii)+\sum_{Ii\neq Aa}S^2_{Aa,Ii}\langle Ii\mid\sum_{J\neq I}z_J\mid Ii\rangle+\sum_{Kk\neq Ii\neq Aa}S^2_{Aa,Kk}J(Kk, Ii)], \quad (18)$$

[10] M. Cohen and C. A. Coulson, Proc. Cambridge Phil. Soc. **57**, 96 (1960).

[11] A. Gold, Phys. Rev. **124**, 1740 (1961).

[12] By a supermolecule is meant the approximation in which the crystal is treated as $H_2^+He_n$, with n large. The wavefunction for this configuration is obtained by constructing molecular orbitals from a linear combination of atomic orbitals.

[13] The reader should note that we have used the approximation

$$\langle Aa\mid T-z_J+\langle J_j\mid g\mid J_j\rangle\mid Ji\rangle\approx S_{Aa,Ji}E_{Ji}.$$

$$E_x=-(1/N')[\sum_{Ii\neq Aa}K(\overline{Aa},Ii)]+(1/N)[\sum_{Ii\neq Aa}K(Aa,Ii)], \quad (19)$$

$$E_T=-(2/N')[\sum_{Ii\neq Aa}S'_{Aa,Ii}\langle\overline{Aa}\mid\sum_{J\neq I}z_J\mid Ii\rangle+\sum_{Ii\neq Aa}\sum_{Kk\neq Ii\neq Aa}S'_{Aa,Kk}\langle\overline{Aa}Ii\mid g\mid KkIi\rangle]+(2/N)[\sum_{Ii\neq Aa}S_{Aa,Ii}\langle Aa\mid\sum_{J\neq I}z_J\mid Ii\rangle+\sum_{Ii\neq Aa}\sum_{Kk\neq Ii\neq Aa}S_{Aa,Kk}\langle AaIi\mid g\mid KkIi\rangle] \quad (20)$$

$$z_J=-Z_Je/(R_J-r);\qquad g=1/r_{12}, \quad (21)$$

$$N=1-\sum_{Ii}S^2_{Aa,Ii}, \quad (22)$$

$$N'=1-\sum_{Ii}S'^2_{Aa,Ii}, \quad (23)$$

$$J(\overline{Aa},Ii)=\langle\overline{Aa}Ii\mid g\mid\overline{Aa}Ii\rangle \quad (24)$$

$$K(\overline{Aa},Ii)=\langle\overline{Aa}Ii\mid g\mid Ii\overline{Aa}\rangle. \quad (25)$$

Finally, it must not be forgotten that the van der Waals interaction between H_2^+ and He changes when the solute H_2^+ is excited. This leads to a change in energy (second-order perturbation theory result)

$$\Delta E_{VdW}=-\sum_I(C_{AI}/R_{AI}^6), \quad (26)$$

$$C_{AI}=\tfrac{4}{9}\sum_{Ii}\sum_{Aa}(R^2)^2_{Ii}(R^2)^2_{Aa}/[(R^2)_{Ii}+(R^2)_{Aa}], \quad (27)$$

$$(R^2)_{Kk}=\langle Kk\mid r^2\mid Kk\rangle-\sum_{k'\neq k}[\langle Kk\mid x\mid Kk'\rangle^2+\langle Kk\mid y\mid Kk'\rangle^2+\langle Kk\mid z\mid Kk'\rangle^2], \quad (28)$$

which is the last term displayed in Eq. (16). As usual, R_{AI} is the internuclear separation of the pair, and in the matrix elements, r, x, y, z are coordinates relative to the nucleus of atom K.

It is worthwhile to mention briefly the nature of the various contributions to the energy shift: E_{at} is the atomic excitation energy corrected for overlap effects, E_c and E_x represent Coulomb and exchange terms, respectively, and E_T is a three-center term involving Coulomb exchange and overlap contributions.

V. NUMERICAL CALCULATIONS AND RESULTS

The He lattice is hexagonal close packed, so that if the H_2^+ molecule ion replaces an He atom, there are 12 nearest neighbors and 30 other atoms close enough to require consideration. It is convenient to subdivide these 42 neighbors of the H_2^+ into four groups. Assuming that the He lattice remains undistorted (lattice parameters $a_0=3.57$ Å, $c_0=5.83$ Å at 2°K) there are 12 neighbors at 6.74 a.u., 6 at 9.54 a.u., 18 at 11.68 a.u., and 6 at 13.49 a.u. Calculations were also made at several other uniformly reduced interatomic distances, in order that the effects of changes in lattice parameter (pressure effects) could be examined. Table II contains a listing of the four sets of distances studied.

TABLE II. Sets of neighbor distances.

	Number of neighbors			
Set	12	6	18	6
1	$6.74a_0$	$9.54a_0$	$11.68a_0$	$13.49a_0$
2	6.61	9.35	11.45	13.22
3	6.47	9.16	11.21	12.95
4	6.34	8.97	10.98	12.68

The analysis outlined in Sec. III was employed to calculate the transition energy, ΔE, for the four sets of lattice distances displayed in Table II. The various contributions to ΔE were calculated exactly, except for the three-center integrals which were evaluated by use of the Mulliken approximation. Previous work on crystalline Ne (Ref. 2) has shown the Mulliken approximation to be quite good, so that we expect no error of note is thereby introduced. The only other assumption made in the numerical calculations is that the nuclear charge of the H_2^+ molecule ion is centered on the internuclear axis and has magnitude $+2\mid e\mid$.

A number of integrals, evaluated with the H_2^+ wavefunctions (9) and (10) and the Green He wavefunction[10]:

$$\psi_{He}=0.18159\chi(1s,2.906)+0.84289\chi(1s,1.453),$$
$$\epsilon_{He}=-0.91792 \text{ a.u.}, \quad (29)$$

are displayed in Table III. The entries in this table refer to the internuclear distances of Set 1, Table II. Finally, the computed transition energies are displayed in Table IV and Fig. 1.

An attempt was made to test the dependence of the spectral shifts on the nature of the wavefunctions employed in the calculations. We have repeated the computations for Set 1 with the simplest He atom wavefunction, i.e., the Slater function $\psi_{He}=(z^3/\pi)^{\frac{1}{2}}e^{-zr}$, characterized by the orbital exponent $z=1.6875$. The results thus obtained are displayed in Table V. It is apparent that the use of the single Slater orbital predicts the correct signs of the various energies, but the magnitudes are seriously in error. Indeed, if the same van der Waals contribution is used as in the more complete calculation, the predicted spectral shift has the wrong sign.

VI. DISCUSSION

We now turn to an examination of the several components of the shift in transition energy. We note that:

(a) The term E_{at} is the excitation energy for the transition including corrections due to the overlap of charge distributions. As expected, a decrease in lattice parameter leading to an increase in overlap causes E_{at} to increase. An examination of Eqs. (17) and (22) and (23), together with the observation that the over-

TABLE III. Several representative integrals (computed with the H_2^+ wavefunctions 9 and 10 and Green's helium wavefunction) for Set 1.[a]

$$(aa \mid bb) = \langle ab \mid g \mid ab \rangle = \iint \psi_A(1)\psi_A(1)\,(r_{12})^{-1}\psi_B(2)\psi_B(2)\,d\tau$$

$$(ab \mid ab) = \langle ab \mid g \mid ba \rangle = \iint \psi_A(1)\psi_B(1)\,(r_{12})^{-1}\psi_A(2)\psi_B(2)\,d\tau$$

$$(A \mid bb) = \int \psi_B(1)\psi_B(1)\,(r_{A1})^{-1}d\tau$$

$$(a, b) = \int \psi_A\psi_B d\tau$$

Function	$R=6.74\ a_0$	$R=9.54\ a_0$	$R=11.68\ a_0$	$R=13.49\ a_0$
$(1s'1s' \mid 1s1s)$	0.14913	0.10536	0.086058	0.074512
$(2p\pi'2p\pi' \mid 1s1s)$	0.14068	0.10136	0.083321	0.072373
$(2p6'2p6' \mid 1s1s)$	0.15705	0.10724	0.086526	0.074453
$(2p6'1s \mid 2p6'1s)$	0.0013106	0.000017479		
$(I \mid 2p6'2p6')$	0.15717	0.10724	0.086526	0.074453
$(I \mid 2p\pi'2p\pi')$	0.14068	0.10136	0.083321	0.072373
$(I \mid 1s', 1s')$	0.14913	0.10536	0.086058	0.074511
$(2p6', 1s)$	0.051903	0.0065147	0.0011798	0.00026432
$(1s', 1s)$	0.0035679	0.00013153		
$(A \mid 2p6'1s)$	0.0096479	0.00084468		
$(1s'1s \mid 1s'1s)$	0.00000			

[a] Those functions belonging to the impurity molecule are primed. Energies in atomic units.

lap in the excited state of the impurity is larger than the overlap in the ground state, shows that

$$[(1/N')\bar{E}_{Aa} - (1/N)E_{Aa}]$$

increases as the lattice constant decreases. Because the overlap is not very large in either state, the remaining terms in (17) make only small contributions to the change in E_{at} with changing lattice parameter.

(b) E_c is the change in Coulomb energy arising from the overlap charge distribution. Again, a decrease in lattice parameter leads to an increase of the overlap charge, hence an increase in the magnitude of E_c. The reader should note from the entries in Table III that the Coulomb integrals and nuclear attraction integrals for the same orbital tend to cancel, so that electron–electron interactions and electron–nucleus interactions are delicately balanced against one another.

(c) Both the change in exchange energy, E_x, and the change in three center contributions, E_T, also depend on overlap. As observed from the entires in Table IV, E_x and E_T change in the same way as do E_{at} and E_c.

(d) The existence of an overlap charge density, larger in the excited state than in the ground state, implies both a negative change in the Coulomb energy and a negative change in the exchange energy. This is a simple consequence of the attraction generated by placing charge between the atoms. On the other hand, charge is then "withdrawn" from the impurity center, thereby increasing its effective nuclear charge. As a consequence of this increase in effective charge, we expect the change in excitation energy to be positive. These arguments lead us to expect $(E_{at})_{\text{solid}} > (E_{at})_{\text{vacuum}}$, $E_c<0$, $E_x<0$, all of which are confirmed on examination of Table IV. It seems very difficult to

TABLE IV. Medium induced spectral shift for H_2^+ in a He matrix calculated using Green's function.[15a]

Set	E_{at} (eV)	E_x (eV)	E_T (eV)	E_c (eV)	ΔE_{VdW} (eV)	E (eV)	$(\bar{E}_{Aa}-E_{Aa})$ (eV)	E_{shift} (eV)
1	17.187	−0.145	+0.222	−0.114	−0.03069	17.119	17.054	0.065
2	17.214	−0.173	+0.271	−0.139	−0.03452	17.138	17.054	0.084
3	17.249	−0.212	+0.336	−0.172	−0.03923	17.162	17.054	0.108
4	17.287	−0.255	+0.411	−0.213	−0.04433	17.186	17.054	0.132

[a] See Ref. 15.

make a simple argument for the three center terms, but in the Mulliken approximation the sign of the change should be the same as that of $(E_{at})_{\text{solid}}-(E_{at})_{\text{vacuum}}$, and for similar reasons. This is also in agreement with the entries of Table IV.

(e) The change in van der Waals energy is small relative to the other energies discussed above. As expected, it is negative and increases as the lattice parameter decreases. Because of the varying signs of the several contributions to the transition energy, the change in van der Waals energy is of the order of

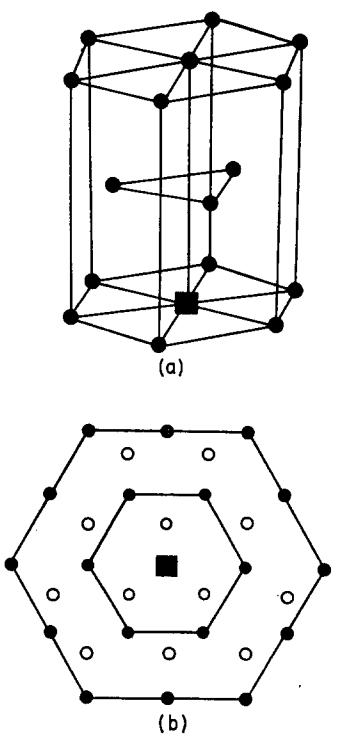

FIG. 1. The crystal structure of the He host lattice: ■ the impurity center; ● neighbors in the same plane; ○ neighbors in adjacent planes.

magnitude of 30% of the total shift in transition energy.

(f) The net change in transition energy is seen to result from a subtle balance between orthogonalization effects, overlap charge effects, and penetration (Coulomb) effects. It is clear that no simple macroscopic characterization of the medium is likely to be successful, despite the superficial simplicity of the trend of excitation energy shift as a function of lattice parameter.

It is now pertinent to examine, in somewhat greater detail than in the Introduction, the nature of continuum dielectric models and other models for the calculation of the transition energy shift. We have already noted that, when overlap may be neglected, the shift

TABLE V. Medium induced spectral shift for H_2^+ in a He matrix calculated using He Slater orbital.

Set	E_{at} (eV)	E_x (eV)	E_T (eV)	E_c (eV)	E (eV)
1	17.149	−0.117	+0.155	−0.085	17.102

in transition energy depends on the difference in dispersion energies between the medium and the ground and excited states of the optical center. Because of the short range of the dispersion interaction, only the properties of the nearest neighbors of the impurity center are important. On the other hand, if the charge distribution of the impurity center overlaps the charge distribution of the surrounding medium, the effects of distant molecules depend on the extent of charge penetration. In the continuum approximation the dielectric medium surrounding a cavity is polarized by the charge remaining in the cavity. The problem may be expressed in a form in which the mean potential exerted on an electron has components from both the parent molecular core and the long range polarization field of the surrounding medium. It is necessary to make the formulation self-consistent because the charge contained in the cavity both depends on the extent of penetration of the surroundings and determines the polarization of the surroundings. It is an interesting observation that when the self-consistent potential problem sketched above is solved for the case of the hydrogen atom in a cavity, it is predicted that there will be blue shifts of the electronic transitions.

Keil and Gold[3] have studied the $1s\rightarrow 2s$ and $1s\rightarrow 2p$ excitation energies of an H atom in crystalline Ar, using methods essentially identical with those employed herein. For a nearest neighbor distance of $7a_0$, the predicted blue shift of the $1s\rightarrow 2p$ transition is 0.4 eV, in

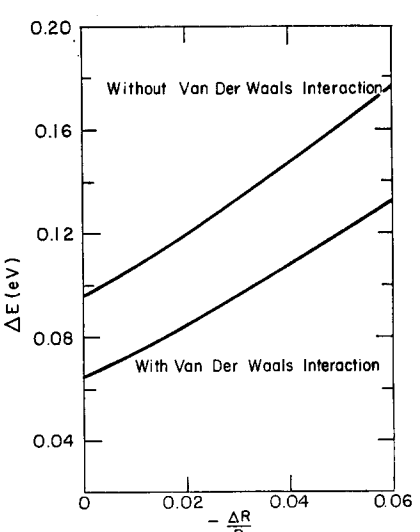

FIG. 2. The dependence of the transition energy of H_2^+ in a He lattice on the lattice parameter.

good agreement with measurements made by Baldini.[14] The predicted blue shift of the $1s \rightarrow 2s$ transition is 2.1 eV, the large value arising because of the large overlap with the surrounding medium in the $2s$ state of hydrogen. Thus, despite the considerable changes in dispersion energy in the H:Ar system (0.5 and 2.2 eV at $7a_0$ for the $1s \rightarrow 2p$ and $1s \rightarrow 2s$ transitions) the sign of the change in the transition energy is determined by the effects of overlap with the surrounding medium. This deduction is in complete accord with our findings for the H_2^+:He system, where overlap with the surrounding medium is much smaller, but still of dominant importance.

Consider, now, the origin of the blue shift in the continuum model. Since the exchange potential, three center terms and the van der Waals energy are all neglected, we see that the continuum model represents a basically different approximation to the calculation of the combined effects of E_{at} and E_c from that studied in this paper. In general terms, the procedure used herein is concerned primarily with overlap and exclusion principal effects, all in the one electron approximation. On the other hand, the continuum model includes polarization of the medium, which may be thought of as a correlation effect. In both cases the removal of charge screening the atomic core leads to an increase of E_{at}. However, the stabilization generated by the potential field of the polarized continuum is not analogous to the favorable change in Coulomb energy arising from the overlap charge density. Now, the polarization energy is less than the increase in E_{at}, so that a blue shift of the transition energy is predicted by the continuum model, but it is not clear that the magnitude of the shift is meaningful. For, the polarization of the medium depends on the extent of charge penetration, which in turn depends on the electronic overlap and required orthogonality to filled shells. Since these effects are not directly included, the polarization energy may be seriously in error. Although it appears that the continuum model mimics the behavior of the real system, we now believe this result to be fortuitous. Thus, the fact that the calculations reported herein predict a blue shift even when E_T and E_x are neglected cannot be meaningfully compared with the similar prediction of the continuum model.

Some comments on the choice of wavefunctions for the calculation of spectral shifts are pertinent. It has been shown that the use of a simple Slater wavefunction for the He atom leads to a serious underestimate of the calculated spectral shift when compared with the result obtained using the Green function[15] (which is a good approximation to the He SCF spin–orbital). It is apparent that the use of a single Slater orbital seriously underestimates the amplitude of the tails of the wavefunctions, leading to serious errors in the estimates of overlap and exchange interactions at typical intermolecular separations, i.e., simple Slater orbitals are inappropriate for the representation of atomic or molecular wavefunctions at large distances. Difficulties arising from the representation of atomic and molecular wavefunctions at large distances have been encountered in many theoretical problems: for example, the calculation of atomic polarizabilities,[16] molecular quadrupole moments,[17] interatomic and intermolecular dispersion forces,[18] charge transfer and exchange interactions in molecular complexes[19] and in aromatic molecular crystals.[20,21] In all these cases the use of SCF wavefunctions for atoms or LCSTO wavefunctions (where the STOS are SCF atomic orbitals) for molecules, leads to an improved description of the behavior of the atomic and molecular wavefunctions at large separations. The calculation of spectral shifts is included in this category of problems involving intermolecular interactions at large distances, and SCF wavefunctions must be used in any attempt to provide quantitative estimates of these effects.

As a result of the calculations presented in this paper, we conclude that any quantitative theory of solvent effects must include detailed consideration of the several consequences of nonvanishing overlap between electron density distributions. There seems no obvious way in which a quantitative theory can be constructed in terms of a simple parameterization using macroscopic properties of the host medium.

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