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Perturbation-theory method of calculating the energies and excitation energies of atomic, molecular, and solid-state systems

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We investigate a general, approximate method for solving the many-electron Schrödinger equation for a molecule or a molecular fragment representing a solid. The method chosen is the unrestricted Hartree-Fock method augmented by a size-consistent many-body perturbation-theory correction. For simplicity, a single-reference development is presented. The extension to multireference formalisms is straightforward if tedious. A few sample results are obtained to illustrate the potential of the method.

I. INTRODUCTION

This paper seeks to examine the utility of Hartree-Fock techniques coupled with perturbation-theory methods in the study of the optical absorption energies of several systems. We have investigated the atoms helium, beryllium, boron, neon, a molecule, methane, and the solids, sodium chloride and potassium chloride. Since very accurate data are available for the atomic cases, these cases can be used to establish the predictive value of the method.

We have calculated multiplet splittings for all of the excited states studied, including several in which an electron is excited into a shell of the same type of symmetry as the ground state. Variational collapse and the proper multiplets are obtained by symmetry projection techniques.

To perform these computations, we use the finite molecular cluster model in the formalism given by Kunz and Klein.[1] Kunz has provided a more general review of this and alternate cluster methods.[2] This method, as used here, applies directly to cluster simulations of extended systems and to free molecules and atoms. Extensions of this method are described in Refs. 1 and 2 and elsewhere.[3,4] In these calculations the unrestricted Hartree-Fock (UHF) method is employed, augmented by direct application of many-body perturbation-theory (MBPT) corrections. We use MBPT in a single or multireference framework as needed. We compute open-shell singlet energies using a back-projection technique. These methods are briefly described below. An open-shell singlet as any singlet state in which all occupied subshells are not fully occupied.

Optical absorption studies have been carried out on alkali halides in the ultraviolet and soft-x-ray regions. It has been hypothesized that certain features in the experimental spectrum can be explained as arising from excitons formed exciting the halogens.[5]

These are two models for excitons. In the Frenkel model, the exciton is treated as an excited state of a single atom perturbed by the environment. In the Wannier model, excitons of large radius are treated by solving Schrödinger's equation for a hydrogenic electron-hole pair in a dielectric material.

Since the halide ion has no simple bound excited states in free space, the Frenkel model cannot apply formally, but an orbital resembling an atomic excited state can be found if one places the ion in a system resembling the positively charged remainder of the lattice.[6] Since the excited state has a moderate radius, details of neighboring atoms must be considered. In the cluster calculation we neglect the motion of the exciton from one site to another.

Several authors have studied excitons in the alkali halides. Dexter[7,8] has made calculation assuming a hole localized at the origin and an electron surrounding it. The electronic function resembles a halide excited state in the region of the halide ion, and a band wave function with an envelope from the hole potential in the rest of the solid. He obtains 7.7 eV for the $3p^54s$ exciton in NaCl, where the experimental value is 7.9 eV, but his wave function is least accurate in the region of the halide ion, where most of the excitonic charge is located. O'Brien and Hernandez[9] and Miyakawa and Oyama[10] have made calculations using the Wannier model on alkali halides. For the Wannier $1s$ exciton in KCl, Miyakawa and Oyama obtain an energy of -1.1 eV and O'Brien and Hernandez obtain -1.2 to -1.5 eV, in contrast to the experimental value of -1.4 eV. These energies are with respect to the interband energy threshold. These calculations do not directly obtain the excitation energies. Song *et al.*[11] have studied the self-trapped exciton, where an electron is bound to an $Cl_2{}^-$ ion in a distorted lattice, in NaCl using techniques similar to ours and obtain an energy of 2.3—2.5 eV as opposed to the experimental value of 2.1 eV. Calculations similar to the ones made in this paper have been made for the x-ray excitons of the alkali metal ions, in the alkali halides.[12]

A model involving charge transfer from the halide ion to the surrounding alkali metal ions has been used to explain the lowest peak in the absorption spectrum, and this model also yields good results for this feature,[13] but a simple charge-transfer model does not describe the higher-energy excitons.

We first investigate the accuracy of the technique used by finding the energy of several atomic excited states. We then extend the method to calculate x-ray-absorption levels in methane. We then investigate certain features in the absorption spectrum of some alkali halides in an attempt to determine by *ab initio* calculation whether certain features in the ultraviolet absorption spectrum may be described as local excitons.

II. THE THEORY

The basic method used to calculate the exciton energy is to take an unrestricted Hartree-Fock (UHF) solution as the starting point and apply Rayleigh-Schrödinger perturbation theory (MBPT). The term unrestricted Hartree-Fock means that the only restrictions on the orbitals are that they are orthonormal and must be spin up or spin down. The many-electron state is not restricted to be an eigenstate of spin, S^2, but is an eigenstate of the z component of spin S_z because the electrons are taken to be either spin up or spin down. We initially approximate our many electron wave function as a single Slater determinant. This is enhanced by perturbation theory to include correlation and by a projection technique to produce eigenstates of S^2. We also make the Born-Oppenheimer approximation. In the Born-Oppenheimer approximation, the Hamiltonian is

$$H=-\tfrac{1}{2}\sum_i \nabla_i^2-\sum_i\sum_I \frac{Z_I}{|\mathbf{r}_i-\mathbf{R}_I|}+\tfrac{1}{2}\sum_i\sum_{j\,(\neq i)}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}+\tfrac{1}{2}\sum_I\sum_{J\,(\neq I)}\frac{Z_IZ_J}{|\mathbf{R}_I-\mathbf{R}_J|}\ . \tag{1}$$

The last term is a constant, since one is neglecting nuclear motions. In this equation, we use atomic units ($e=\hbar=m=1$, energy 1 hartree$=27.2$ eV). Here also Z_I is the atomic number of the nucleus at site $\mathbf{R}_I$. If one chooses the wave function to be a single Slater determinant made up of single-electron orbitals $\phi(i)$, where $\phi(i)=\phi_i(\mathbf{r})\alpha$ or $\phi(i)=\phi_i(\mathbf{r})\beta$, then

$$\langle H\rangle=\sum_i\int d\tau\,\phi_i^*(\mathbf{r})\left[-\tfrac{1}{2}\nabla^2-\sum_I\frac{Z_I}{|\mathbf{r}-R_I|}\right]\phi_i(\mathbf{r})+\sum_{\substack{i,j\\ i<j}}\left[\int d\tau_1\int d\tau_2\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}\,|\phi_i(\mathbf{r}_1)|^2\,|\phi_j(\mathbf{r}_2)|^2-\delta_{m_{s_i},m_{s_j}}\int d\tau_1\int d\tau_2\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}\phi_i^*(\mathbf{r}_1)\phi_j^*(\mathbf{r}_2)\phi_j(\mathbf{r}_1)\phi_i(\mathbf{r}_2)\right]\ . \tag{2}$$

If one requires $\delta\langle H\rangle=0$ and $\langle\phi_i\,|\,\phi_j\rangle=\delta_{ij}$ one finds

$$-\tfrac{1}{2}\nabla_1^2\phi_i(\mathbf{r}_1)-\sum_I\frac{Z_I\phi_i(\mathbf{r}_1)}{|\mathbf{r}_1-\mathbf{R}_I|}+\left[\sum_j\int d\tau_2\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}\,|\phi_j(\mathbf{r}_2)|^2\right]\phi_i(\mathbf{r}_1)-\sum_j\delta_{m_{s_i},m_{s_j}}\left[\int d\tau_2\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}\phi_j^*(\mathbf{r}_2)\phi_i(\mathbf{r}_2)\right]\phi_j(\mathbf{r}_1)=\varepsilon_i\phi_i(\mathbf{r}_1)\ , \tag{3}$$

which is the UHF equation.[14] Adams[15] and Gilbert[16] and Kunz[1–4,17] have discussed the formalism by which a system may be partitioned into a cluster and its environment such that the localization of orbitals in the cluster can be ensured. This formalism enables one to treat local excitations in a solid without explicit consideration of 10^{23} electrons. We use the Hartree-Fock equation modified according to the Adams-Gilbert formalism. The Hartree-Fock equation can be written as

$$F\phi_i=\varepsilon_i\phi_i\ , \tag{4}$$

where F is called the Fock operator and the ϕ are the orbitals of the system. One can divide this operator into two parts

$$F=F_A+U_A\ , \tag{5}$$

where F_A is the interaction within a region A and U_A is a potential due to the environment. Then

$$(F_A+U_A-\rho W\rho)\phi_i=\Pi_i\phi_i\ , \tag{6}$$

where Π_i is the eigenvalue of the Adams-Gilbert-Kunz equation. This eigenvalue has no direct physical interpretation. The first-order density matrix ρ is defined as

$$\rho=\sum_{\substack{i,j\\ \text{occ}}}\phi_i s_{ij}^{-1}\phi_j^\dagger$$

with S_{ij} the overlap matrix $\langle\phi_i\,|\,\phi_j\rangle$, and W is chosen to effect localization of orbitals within region A. For an ionic system,

$$U_A=V_M+V_S\ , \tag{7}$$

where V_M is the Madelung contribution and V_s are short-range effects outside region A. Choose $W=V_S$ and

$$(F_A+V_M)\phi_i=\pi_i\phi_i-V_S\phi_i+\rho V_S\rho\phi_i\ . \tag{8}$$

Now $\rho\phi_i=\phi_i$. If proper localization has been effective,

$\rho V_S\phi_i = V_S\phi_i$ to first order in overlap in the limit of self-consistency, and the UHF equation becomes

$$(F_A+V_M)\phi_i=\pi_i\phi_i\ . \qquad (9)$$

The UHF method neglects correlation by definition. That is, it is a form of mean-field theory. It has been shown that for large systems, such as we may wish to consider, one must use a correlation method which is size consistent (extensive).[18,19] One such method is the MBPT method. One partitions the exact Hamiltonian H into a simple Hamiltonian H_0 whose eigenvalues and eigenfunctions are known, and a perturbation V is chosen so that

$$H\equiv H_0+V\ . \qquad (10)$$

In our case we chose H_0 to be the sum of the one-body Fock operators for the n-electron system. Let us call the particular state we are obtaining ψ_0 with the energy, E_0; both ψ_0 and E_0 being unknowns. Now, one has

$$H\psi_0=E_0\psi_0=(H_0+V)\psi_0\ .$$

Since the eigenfunction, ϕ_i, with eigenvalue W_i of H_0 are known, one may use these to obtain E_0 and ψ_0. Consider that

$$(H_0-W_0)\psi_0=(E_0-V-W_0)\psi_0\ . \qquad (11)$$

Now we must have W_0 nondegenerate in this single reference approach. One may take a limited inverse of (H_0-W_0), provided that one operates only on a function which has no projection on to ϕ_0. This is easily accomplished by using P, the projector onto ϕ_0,

$$P=|\phi_0\rangle\langle\phi_0|\ .$$

That is multiplying Eq. (11) by $(1-P)$, one finds

$$\begin{aligned}(1-P)(H_0-W_0)\psi_0&\equiv(H_0-W_0)(1-P)\psi\\ &=(1-P)(E_0-V-W_0)\psi_0\end{aligned}$$

or

$$\psi_0-P\psi_0=(H_0-W_0)^{-1}(1-P)(E_0-V-W_0)\psi_0\ . \qquad (12)$$

At this point, even if the ϕ's form an orthonormal set, the normalization of ψ_0 is arbitrary. Define it to be such that

$$\langle\psi_0|\phi_0\rangle=1\ .$$

This is called intermediate normalization. If this is done, then one finds (12) reducing to

$$\phi_0=\psi_0-(H_0-W_0)^{-1}(1-P)(E_0-V-W_0)\psi_0\ ,$$

which may be formally solved for ψ_0,

$$\psi_0=[1-(H_0-W_0)^{-1}(1-P)(E_0-V-W_0)]^{-1}\phi_0\ .$$

This in turn results in a power series for ψ_0,

$$\begin{aligned}\psi_0=\phi_0&+(H_0-W_0)^{-1}(1-P)(E_0-V-W_0)\phi_0\\ &+\cdots+[(H_0-W_0)^{-1}\\ &\qquad\times(1-P)(E_0-V-W_0)]^n\phi_0+\cdots\ . \qquad (13)\end{aligned}$$

From this, one may develop an expression for the energy E_0 as well. Consider

$$\langle\phi_0|H\,|\psi_0\rangle=\langle\phi_0|E_0\,|\psi_0\rangle$$

or

$$\langle\phi_0|H_0\,|\psi_0\rangle+\langle\phi_0|\,V\,|\psi_0\rangle=\langle\phi_0|E_0\,|\psi_0\rangle\ .$$

Using the chosen normalization and the known eigenvalue relations, one finds immediately,

$$W_0+\langle\phi_0|\,V\,|\psi_0\rangle=E_0\ ,$$

or

$$E_0=W_0+\langle\phi_0|\,V\,|\psi_0\rangle\ . \qquad (14)$$

To proceed, one replaces ψ_0 in Eq. (14) with its expansion in Eq. (19). This yields

$$\begin{aligned}E_0=W_0&+\langle\phi_0|\,V\,|\phi_0\rangle+\langle\phi_0|\,V(H_0-W_0)^{-1}(1-P)(E_0-V-W_0)\,|\phi_0\rangle+\cdots\\ &+\langle\phi_0|\,V[(H_0-W_0)^{-1}(1-P)(E_0-V-W_0)]^n\,|\phi_0\rangle+\cdots \qquad (15)\end{aligned}$$

This is not yet complete. Let us construct the matrix of V in terms of the n-electron basis vectors ϕ_i, Then,

$$V_{00}=\langle\phi_0|\,V\,|\phi_0\rangle\ ,$$

for example. Equation (15) is not extensive due to the presence of the unknown E_0 occurring in the right-hand side of this equation. The correct solution is to replace E_0 by its first-order expression.[18] Let $E_0\approx W_0+V_{00}$. If this is done one finds (exactly)

$$\begin{aligned}E_0=W_0+V_{00}&+\langle\phi_0|\,V(H_0-W_0)^{-1}(1-P)(-V)\,|\phi_0\rangle+\langle\phi_0|\,V[(H_0-W_0)^{-1}(1-P)(V_{00}-V)]^2\,|\phi_0\rangle+\cdots\\ &+\langle\phi_0|\,V[(H_0-W_0)^{-1}(1-P)(V_{00}-V)]^n\,|\phi_0\rangle+\cdots\ . \qquad (16)\end{aligned}$$

This is the desired form and is a particular form of Rayleigh-Schrödinger perturbation theory. If one stops at second order, one may see that,

$$E_0=W_0+V_{00}+\sum_{I\,(\neq 0)}\frac{V_{0I}V_{I0}}{W_0-W_I}=W_0+V_{00}+E_0^{(2)}\ . \qquad (17)$$

Bartlett and co-workers have shown this to typically obtain 90% of the correlation energy in a given basis set.[20]

The structure of the Hamiltonian is such that if state ψ_I differ from ψ_J by three or more one-electron orbitals then $V_{IJ}\equiv 0$. Furthermore, as a consequence of Brillouin's theorem,[18] if ψ_J differs by only one orbital from ψ_0 then

$$V_{0J}=V_{J0}=0\ .$$

The matrix element V_{00} or generally V_{II} is not zero and is usually large. Furthermore if ψ_I differs from ψ_0 in that orbitals ϕ_i and ϕ_j in ψ_0 are replaced by ϕ_a and ϕ_b in ψ_J one has

$$W_0-W_I=\epsilon_i+\epsilon_j-\epsilon_a-\epsilon_{b'}$$

and

$$\begin{aligned}V_{0I}&=\langle\phi_i\phi_j\,|\,g\,|\,\phi_a\phi_b\rangle-\langle\phi_i\phi_j\,|\,g\,|\,\phi_b\phi_a\rangle\\&=g_{ijab}-g_{ijba}\ ,\end{aligned}\tag{18}$$

where $g=e^2/|\mathbf{r}-\mathbf{r}'|$. Thus Eq. (17) becomes

$$E_0=W_0+V_{00}+\sum_{\substack{i,j\,(\text{occ})\\ i>j}}\ \sum_{\substack{a,b\,(\text{virt})\\ a>b}}\frac{(g_{ijab}-g_{ijba})^2}{\epsilon_i-\epsilon_j-\epsilon_a+\epsilon_b}\ .\tag{19}$$

It is possible to use the fact that in general

$$V_{II}\gg V_{IJ}$$

for all I and J to improve Eq. (19). Consider the next term in Eq. (17), the third-order term

$$\begin{aligned}E_0^{(3)}&=\langle\phi_0\,|\,V[(H_0-W_0)^{-1}(1-P)(V_{00}-V)]^2\,|\,\phi_0\rangle\\&\equiv\langle\phi_0\,|\,V(H_0-W_0)^{-1}(1-P)(V_{00}-V)(H_0-W_0)^{-1}(1-P)(-V)\,|\,\phi_0\rangle\\&\equiv-V_{00}\sum_{I\,(\neq 0)}\frac{V_{0I}V_{0I}}{(W_0-W_I)^2}+\sum_{I\,(\neq 0)}\sum_{J\,(\neq 0)}\frac{V_{0I}V_{IJ}V_{J0}}{(W_0-W_I)(W_0-W_J)}\ .\end{aligned}\tag{20}$$

This has a dominant part given when $I=J$ in the second term and is

$$\begin{aligned}E^{(3)}\approx&\sum_{I\,(\neq 0)}\frac{V_{II}}{(W_0-W_I)}\,\frac{V_{0I}V_{I0}}{(W_0-W_I)}\\&-V_{00}\sum_{I\,(\neq 0)}\frac{V_{0I}V_{I0}}{(W_0-W_I)^2}\end{aligned}$$

or

$$E_0^{(3)}\approx\sum_{I\,(\neq 0)}\left[\frac{V_{II}-V_{00}}{W_0-W_I}\right]\frac{V_{0I}V_{I0}}{W_0-W_I}\ .\tag{21}$$

In fact, each order has a dominant term given by

$$E_0^{(n)}\approx\sum_{I\,(\neq 0)}\left[\frac{V_{II}-V_{00}}{W_0-W_I}\right]^{n-2}\frac{V_{0I}V_{I0}}{W_0-W_I}\ .\tag{22}$$

Therefore if one ignores all but the largest term at each order, one has

$$E_0\simeq W_0+V_{00}+\sum_{I\,(\neq 0)}\frac{V_{0I}V_{I0}}{W_0-W_I}\left[\sum_{j=0}^{\infty}\left[\frac{V_{II}-V_{00}}{W_0-W_I}\right]^j\right]\ .$$

If, as is usually the case,

$$\left|\frac{V_{II}-V_{00}}{W_0-W_I}\right|<1\ ,$$

one finds

$$\begin{aligned}E_0\simeq&\ W+V\\&+\sum_{I\,(\neq 0)}\frac{V_{0I}V_{I0}}{W_0-W_I}\left[\frac{1}{1-(V_{II}-V_{00}/W_0-W_I)}\right]\ .\end{aligned}\tag{23}$$

This is a many-body form of the well-known denominator insertion trick used in many-body physics.[18] In practice one evaluates both Eqs. (17) and (23) to see if the denominator insertion has a small effect on the second-order term. If it is small then it is likely the perturbation expansion has converged.

If, on the other hand, this insertion has a large effect on $E_0^{(2)}$ then it is likely that one has a poorly convergent series and either a better H_0 or basis set is needed. It is also noted the choice of which orbitals go into ϕ_0 is arbitrary, therefore this method applies equally well to all eigenstates of H, not just the ground state. Provided that Eq. (13) converges, one may compute any state of H this way.

The derivation of the UHF equation does not specify that the occupied orbitals must be chosen in any particular manner. In principle, one can use the wave function of an excited state. In practice, variational collapse, to the ground state or some other low-energy state, frequently occurs when one attempts to calculate an excited state in a variational calculation.[21] It has been proven difficult to calculate the energies of these states accurately, even for simple cases such as the He $1s\,2s$ singlet.[22] Excited states are located at local energy minima in parameter space. If these minima are shallow, the excited state may be unstable with respect to variation of the parameters, and it will be difficult to converge the state.

The technique recently developed by A. B. Kunz has been used to enable convergence in an excited state solution of the Hartree-Fock equations. The ground-state solution is found by standard techniques. In addition to the orbitals occupied by electrons, a number of unoccupied orbitals, called virtual orbitals, are created. The method of Kunz has three steps.

(1) One of the ground-state orbitals is selected to be depopulated and a virtual orbital is populated in is place.

(2) A new Fock operator is generated from this set of orbitals and it is solved for a new set of orbitals and eigenvalues.

(3) The state having the greatest overlap with the orbi-

tal depopulated in step (1) is depopulated and steps (2) and (3) are repeated until convergence.

Every system we have studied except boron involves a closed-shell ground state. The systems in question have low-lying excited states which can be described as an electron-hole pair in either the triplet or the singlet spin state. The triplet spin state can readily be found by the UHF method as it is the ground state for $S_z=1$. In the UHF formalism it is impossible to specify an excited state that is pure singlet so a back-projection technique is used. With back projection one can derive the energy of a pure singlet state from the known energy of a pure triplet state and the known energy and expectation value of S^2 of the triplet contaminated singlet state actually obtained. The energy of the pure singlet state is found in this limit to be

$$E_S=E_0-\frac{S(S+1)(E_T-E_0)}{1-S(S+1)} \tag{24}$$

where E_0 is the energy of the calculated state, $S(S+1)$ is the calculated S^2, and E_T is the triplet energy. Although one does not know the singlet-state wave function, one can, in principle, calculate the expectation of any operator T in the singlet state, given that $[H,T]=0$ and $[H,S^2]=0$.

III. METHODS

The methods used to solve the UHF equation is that of Roothaan.[23] The atomic basis sets used are based on those of Huzinaga[24] although certain modifications have been made. Basis functions have been added to describe the excited states. The exponents for these functions are found by minimizing the UHF energy of the triplet excited state. Basis functions have also been added to increase the magnitude of the perturbation energy found. Some contractions have been made in the basis sets either to enable convergence or to make calculations proceed more rapidly. For molecules and solids the LCAO technique was used. The atomic sets used for potassium, sodium, and hydrogen atom of methane were developed using the ANALHF code. A polarization functions were added to the hydrogen set following Meyer.[25] The chloride *d* state was represented with a set of *d* functions for the chlorine atom from Rappe *et al.*[26] while the rest of the chlorine set is from Huzinaga.

Integrals between the Gaussian basis functions used to expand the orbitals have been calculated using the POLYATOM code. The UHF and MBPT codes developed by Kunz and his co-workers have been used to find the Hartree-Fock energy and perform the perturbation calculation. Integrals of size 10^{-9} hartree were retained and self-consistence to 10^{-6} hartree was achieved.

The alkali halide crystals were modeled as a cluster of one chloride ion surrounded by six alkali-metal ions in a charge-neutral array of point charges. The alkali-metal basis sets were heavily contracted in free space. The lattice parameter of NaCl at 86 K was taken from the data of James and Firth.[27] The lattice parameter of KCl at 77 K was found by extrapolation from the lattice parameter at 298 K given by Donnay *et al.*,[28] using coefficients of linear expansion given by White.[29]

In the alkali halides it proved necessary to make corrections for the polarization of the ions surrounding the central halide ion caused by the quadrupole moment of the excited state. Polarization corrections were carried out by the method of Mott and Littleton[30] using polarizabilities taken from Tessman *et al.*[31] A distribution of point

TABLE I. Summary of results. All energies are in eV. (T, triplet; S, singlet).

Material	State	UHF energy	Total energy	Experimental energy
He	$1s2s$ (T)	19.04	19.8	19.82(34)
He	$1s2s$ (S)	19.88	20.58	20.61(34)
Be	$2s3s$ (T)	5.69	6.35	6.46(34)
Be	$2s3s$ (S)	6.00	6.56	6.78(34)
B	$2s^23s$	4.89	4.90	4.96(35)
B	$2s^23p$	5.92	5.84	6.03(35)
Ne	$2p^53s$ (T)	15.00	16.44	16.65(34)
Ne	$2p^53s$ (S)	15.18	16.75	16.85(34)
Ne	$2p^53p$ (T)	16.78	18.33	
Ne	$2p^53p$ (S)	17.27	18.56	
CH_4	$1s3s$ (T)	286.68	286.88	
CH_4	$1s3s$ (S)	287.03	287.27	287.2(36)
CH_4	$1s3p$ (T)	287.92	288.11	
CH_4	$1s3p$ (S)	288.06	288.24	288.3(36)
NaCl	$3p^54s$ (T)	8.33	8.02	7.9(5)
NcCl	$3p^54s$ (S)	8.51	8.30	8.1(5)
NaCl	$3p^53d(xy)$ (T)	9.59	10.22	10.3(5)
NaCl	$3p^53d(xy)$ (S)	9.62	10.26	10.3(5)
NaCl	$3p^53d(zz)$ (T)	9.23	9.62	10.3(5)
NaCl	$3p^53d(zz)$ (S)	9.25	9.64	10.3(5)
KCl	$3p^54s$ (T)	7.84	7.62	7.8(5)
KCl	$3p^44s$ (S)	7.98	7.76	7.9(5)

charges was used to represent the exciton. Charges in an s state were located at the origin, charges in a p state or a d state were located at the known radius of the chloride ion in NaCl and KCl.

These calculations were made on a Floating Point Systems FPS 164 scientific computer with a Digital Equipment Corporation VAX11/750 host machine. Limitations on the amount of computer time available prevented an all-electron perturbation calculation on KCl, and so instead only the electrons in the $n=3$ shell of the chloride ion were considered in the perturbation calculation. Tests on neon have shown that elimination of the core levels and higher virtuals in this calculation makes little difference to the final result.

IV. RESULTS

The results of this investigation are tabulated in Table I. The energy levels calculated in the UHF-MBPT-polarization approximation appear to be within 0.2 eV of the experimental levels for all atomic and molecular cases. Singlet-triplet splittings appear to be accurate to within 0.1 eV.

One point frequently brought up in connection with the UHF method is that the states we call triplet states are not exact eigenstates of S^2. Our calculated values of the spin in the triplet state were between 1.0000 and 1.0005 for atomic cases, 1.01 for methane, and between 1.000 and 1.002 for the alkali halides. Since S_z is chosen equal to 1 it seems reasonable to identify these states as triplet, since it is unlikely that a mixture of eigenstates of S^2 with substantial contributions form states with eigenvalues of S^2 greatly different from 2 would give a value of S so close to the expected value for a pure triplet state.

The experimental data for the alkali halide crystals are shown in Table I. The levels hypothesized to be the result of a $3p^5 3d$ exciton, as theoretically predicted, lie in the region covered by the shoulder above the $p \rightarrow s$ exciton.

No variational collapse is observed in any of these systems. Our computed value for the He $1s\,2s$ singlet energy is 0.7562 hartree. Fraga and Brissa[32] obtain 0.7461 hartree. Other workers[22,33] have not reported the ground-state energy they obtain but give absolute energies for the excited state comparable to our result.

V. CONCLUSIONS

These methods are being applied to study the electromagnetic line spectrum of several atoms, molecules and of excitons in solids. These calculations, which in fact use a multireference framework permitting resolution of multiplied structure, have been performed for the outer electron shell in atomic He, Be, B, Ne, for the $1s$ shell of C in the CH_4 molecule, and for the formation of the valence exciton in NaCl and KCl.[34-36] The spectral levels are seen to be in fine agreement with experiment both as to position, typically errors are of 2% or less, and with respect to multiplet splittings. It is also seen that the MBPT results are a great improvement on the UHF ones. This is especially true with respect to multiplet splittings. The authors conclude this is an effective and accurate way of studying the electromagnetic line spectra of atoms, molecules and solids.

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