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Deep Impurity States in Molecular Crystals: The Optical Excitation of a Substitutional Argon Atom in Crystalline Neon

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The calculation of the first electronic transition of an argon-atom impurity in a neon lattice is carried out in the Heitler-London scheme. The energy of this transition is taken to be the energy of the argon atomic transition, plus the correction to the SCF 4*s* orbital energy due to the presence of the crystal. The modification to the SCF 4*s* orbital is accomplished by the addition of charge-transfer functions on neighboring neon atoms. It is shown that the choice of the SCF atomic function is a very bad starting point for these systems.

A general method for choosing basis functions for bound systems is presented. It is shown that for many cases a suitably chosen "model Hamiltonian" may be appropriate to a more complex system, and the case of a dielectrically screened hydrogenic "model Hamiltonian" is worked out for Ar–Ne.

I. INTRODUCTION

A TREATMENT of the properties of an atom or molecule present as an impurity in a host crystal may be built on several different approximation schemes. In one such scheme, it is assumed that the medium only slightly perturbs the manifold of states of the solute. In the earliest work, the effects of the surrounding medium are represented either in terms of macroscopic parameters (dielectric constant and/or polarizability–dispersion energy theories) or, for special cases, in terms of the splittings induced by the crystalline field of the ordered environment (ligand-field theory). The first group of theories is useful only when the wavefunctions characterizing both the excited and ground states of the solute do not overlap the wavefunctions describing the surrounding solvent molecules. The crystal-field theories are primarily of use in describing the removal of degeneracies present in the free atom or molecule and, thereby, for the calculation of level splittings. They are less satisfactory for the calculation of absolute energy-level shifts due to changes in environment. Thus, neither of the descriptions cited is adequate for the many cases in which the wavefunction of the excited state of the solute extends far into the surrounding medium. Now, from the work of Gold,[1,2] of Keil and Gold,[3] and of Sun, Rice, and Jortner,[4] it is found that the change in excitation energy of a solute atom or molecule represents only the delicate net balance between large changes in Coulomb energy, exchange energy, etc. Indeed, the change in excitation energy of the solute is often very much smaller than any of the component energy changes and, also, very much smaller than can be accounted for by taking into account only the states of the isolated atom or molecule. That is, the presence of the surrounding medium may lead to an effective delocalization of the charge density of the excited solute, thereby greatly altering the excitation energy.

A fundamentally different approach, much discussed in the literature of solid-state physics, is to regard the impurity as a perturbation on the manifold of states of the crystalline host. When the perturbation may be regarded as weak and slowly varying in space, it is possible to show that the impurity levels are hydrogenic and that the surrounding medium dielectrically screens the electron–parent core interaction. This description is applicable to donor states in Ge and Si, but even in these cases where the dielectric constant is large and the binding energies of the impurity small (Ge: $\epsilon=16$, $E_{\text{ion}}{}^{\text{imp}}\sim0.01$ eV, Si: $\epsilon=12$, $E_{\text{ion}}{}^{\text{imp}}\sim0.03$ eV) appreciable corrections are required to the lowest calculated excitation energy of the impurity. The theory fails for the lowest excitation of the impurity because the electron–parent core interaction deviates from the dielectrically screened Coulomb potential near the impurity site. Of more importance for the problem we consider herein, the hydrogenic Hamiltonian effective-mass theory appears (superficially) inapplicable to the description of deep impurity states.

In this paper we report a theoretical analysis of the electronic transition between the ground state and the first excited state of the system consisting of an argon atom in a neon lattice. Two approaches are considered, a supermolecule formalism and a pseudopotential formalism. As in other analyses, we use the static-lattice approximation and neglect the effects of nuclear vibrations. This approximation is expected to be satisfactory for the calculation of the location of absorption lines, but will not yield useful information on linewidths, vibronic coupling phenomena, etc. There have been two previous studies of the lowest electronic excitation of an argon atom in a neon lattice.[1,2] In both instances it is assumed that a product of isolated-atom wavefunctions is an adequate first-order electronic wavefunction for the crystal. The calculations differ in

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[1] A. Gold, J. Phys. Chem. Solids **18**, 218 (1961).

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

[3] T. Keil and A. Gold, Phys. Rev. **136**, A252 (1964).

[4] H. Sun, S. A. Rice, and J. Jortner, J. Chem. Phys. **41**, 3779 (1964).

the mathematical techniques used to orthogonalize the wavefunction of the excited Ar atom to the closed shells of the surrounding Ne atoms. The first calculation suffered from the lack of convergence of the symmetric orthogonalization procedure carried out.[1] When a Schmidt orthogonalization procedure is used,[2] the calculation leads to the prediction of a large blue shift (~4 eV) of the first optical transition relative to the same transition in the free atom. Direct measurement of this transition leads to the very much smaller blue shift of 0.9 eV.[5]

In a recent study of the optical spectrum of crystalline Ne, using the supermolecule formalism, it was found that charge delocalization in the excited state leads to a large decrease in the orbital energy of the excited state. In essence, the inclusion of charge-transfer states is a mechnism for introducing more flexibility into the basis set describing the excited state of the crystal and is to be understood as defining an approximation function with the extent of delocalization determined by the variational principle. In this paper, when the supermolecule formalism is used, a similar representation of the excited-state wavefunction is employed and the resulting orbital energies and wavefunctions reported. Since we neglect any changes of the electronic wavefunctions of the surrounding Ne atoms due to the presence of an excited Ar atom, consistency requires that we also omit shifts due to bulk dielectric effects and to changes in dispersion energy. As in the study of the optical spectrum of crystalline Ne, it is found that charge delocalization leads to a decrease of orbital energy such that the predicted transition energy is in much better agreement with the observed transition energy[5] [ΔE(calc.) = 13.1 eV, ΔE(obs.) = 12.7 eV].[6]

If charge delocalization is the property that must be properly handled in problems of the type considered herein, then it is pertinent to examine methods other than the use of charge-transfer states to represent charge delocalization. For this reason we have also examined the use of a pseudopotential and model Hamiltonian formalism, with the model Hamiltonian chosen to be of the dielectrically screened hydrogenic type. It is found that the charge delocalization and wavefunction described by the pseudopotential formalism lead to a minimum orbital energy for a dielectric constant not very different from that characteristic of pure neon. We are thereby led to the conclusion that when the radius of the lowest hydrogenic orbit is large relative to the size of the Wannier function describing the localized state, the dielectrically screened hydrogenic model Hamiltonian leads to a valid description.

II. METHOD OF CALCULATION

A. Some Comments on the Supermolecule Formalism

The approach used in this calculation is so similar to that employed previously that the reader is referred to the earlier work for the computational details.[7] Briefly, the formalism is as follows: The excited state is taken to be representable in the form

$$\Psi_e=\mathcal{A}\psi_{Aa}\varphi_{Aa}'\prod_{i(\neq a)}\varphi_{Ai}\varphi_{Ai}'\prod_{J(\neq A)}\prod_{j}\varphi_{Jj}\varphi_{Jj}', \tag{1}$$

where the capital letters refer to the nuclear sites, A being reserved for the "central atom" (in this case the argon atom and in general the atom in an excited state). The small letters refer to the particular functions, $1s$, $2s$, $\cdots$, while the primes denote an α spin state, with the absence of primes referring to the β spin state. As usual, $\mathcal{A}$ is the antisymmetrization operator.[8] The function Ψ_e is not a pure spin state. The true energy of the $^{1,3}P$ crystal state will then be different from that calculated with Ψ_e by an amount

$$\pm(\psi_{Aa}(1)\varphi_{Aa}(1)\mid r_{12}^{-1}\mid\psi_{Aa}(2)\varphi_{Aa}(2)). \tag{2}$$

This energy, which is of the order of magnitude of 0.2 eV, is omitted from our analysis, as is the effect of spin–orbit coupling. A more complete analysis would have to include (2), but it would be inconsistent to retain it without also including the first-order changes in van der Waals energy as well as other corrections of the same order of magnitude. Since we do not at present understand how to compute dispersion energies in strongly overlapping atomic configurations, all such terms have been neglected.

The function ψ_{Aa} is taken to be

$$\psi_{Aa}=U(|\mathbf{O}|)\tilde{\chi}_{Aa}+U(|\boldsymbol{\beta}_1|)\sum_{N=1}^{12}\tilde{\chi}_{Nn}$$
$$+U(|\boldsymbol{\beta}_2|)\sum_{M=1}^{6}\tilde{\chi}_{Mn}+U(|\boldsymbol{\beta}_3|)\sum_{P=1}^{24}\tilde{\chi}_{Pn}, \tag{3}$$

where the functions $\tilde{\chi}_{Aa}$, $\tilde{\chi}_{Nn}$, $\cdots$, represent Schmidt orthogonalized SCF excited orbitals,

$$\tilde{\chi}_{Aa}=(1/\eta_A^{\frac{1}{2}})\{\bar{\varphi}_{Aa}-\sum_{Jj}\langle\overline{Aa}\mid Jj\rangle\varphi_{Jj}\},$$
$$\eta_A=\{1-\sum_{Jj}\langle|\overline{Aa}\mid Jj\rangle^2\}, \tag{4}$$

and we use $\bar{\varphi}_{Aa}$ for the SCF $4s$ function of an isolated argon atom. The number $\langle\overline{Aa}\mid Jj\rangle$ is the overlap integral $\int\bar{\varphi}_{Aa}\varphi_{Jj}d\tau$, where φ_{Jj} is the neon ground-state

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[5] G. Baldini, Phys. Rev. **137**, A508 (1965). We focus our attention on the ^1P state of the crystal, which is assumed to be the higher-energy transition of the ^1P, ^3P doublet.

[6] In the earlier work by Gold (Ref. 1) and in a private communication from him, the change in the van der Waals energy due to excitation has been estimated as −0.4 or −0.5 eV. The sign and order of magnitude of this estimate tends to improve agreement between calculation and experiment.

[7] S. Webber, S. A. Rice, and J. Jortner, J. Chem. Phys. (to be published).

[8] $\mathcal{A}=(N!)^{-\frac{1}{2}}\Sigma_{P_\nu}(-1)^\nu P_\nu$, where P_ν exchanges the νth pair of electrons.

orbital j on the Jth nucleus. $\tilde{\chi}_{Nn}$, $\tilde{\chi}_{Mn}$, and $\tilde{\chi}_{Pn}$ all refer to functions analogous to (4),

$$\tilde{\chi}_{Mn}=(1/\eta_M^{\frac{1}{2}})\{\bar{\varphi}_{Mn}-\sum_{Jj(=Aj)}\langle\overline{Mn}\mid Jj\rangle\varphi_{Jj}\},$$

$$\eta_M=\{1-\sum_{Jj(=Aj)}\langle\overline{Mn}\mid Jj\rangle^2\}, \tag{5}$$

where $\bar{\varphi}_{Mn}$ is the SCF $3s$ orbital for an isolated neon atom. The sets of functions $\tilde{\chi}_{Nn}$, $\tilde{\chi}_{Mn}$, $\tilde{\chi}_{Pn}$ are classified with respect to the shells of atoms surrounding the Ar atom. In a face-centered-cubic crystal there are 12 nearest neighbors to any given atom, then a shell of six atoms followed by a shell of 24 atoms, and so forth.[9] The argon atom is expected to create a symmetric distortion of the Ne lattice, and the spherically symmetric functions $\tilde{\chi}_{Nn}$, $\tilde{\chi}_{Mn}$, $\cdots$, are thereby assumed to mix equally if they belong to the same shell. If $\boldsymbol{\beta}_j$ is the vector from the central atom to the jth shell and $N(|\boldsymbol{\beta}_j|)$ is the number of atoms in the jth shell, then the general expression defining the "supermolecule" wavefunction used in this paper is

$$\psi_{Aa}=\sum_{j=0}U(|\boldsymbol{\beta}_j|)\sum_{M=1}^{N(|\boldsymbol{\beta}_j|)}\sum_n\tilde{\chi}_{Mn}\alpha_n, \tag{6}$$

where M refers to the Mth nuclear site of the jth shell and n is the particular SCF excited state which is orthogonalized to the neon and argon core orbitals. The index n may change from shell to shell; for the case described herein $n=a$ represents the Ar $4s$ function for the $j=0$ shell and represents the Ne $3s$ function for all other shells. The sum over j is carried up to $j=3$ for the case studied in this paper. The reader should note that the wavefunction (6) is similar to that introduced by Wannier[10]; for the case of a pure crystal, the relationship between (6) and a Wannier function is discussed in Appendix I of our previous paper.[11] The basic difference between the basis set (6) and the set of Wannier functions is the following: Wannier employs the full sum over j but uses an approximate means to diagonalize the resulting energy matrix, while in the present treatment the sum is truncated but an attempt is made to evaluate all matrix elements exactly and diagonalize the energy matrix directly. The Wannier approach is easier to use for the higher excited states of the crystal, but leads to large central-cell corrections because of the neglected matrix elements. Under many conditions the Wannier description of the lowest excited state is inadequate because of the neglect of off-diagonal charge distributions interacting with the central "hole." The relevant domains of applicability of these two complementary approaches can only be determined by direct calculation, but such calculations are fraught with difficulty. Also, the use of Wannier functions requires the definition of Bloch states for the crystal, but such states are not easily found for the case that the impurity represents a strong perturbation to the electronic structure of the crystal. Indeed, the direct diagonalization procedure used herein is considerably easier to apply to the argon–neon case.

The calculation is, in principle, quite easily carried out: the matrix of the different functions

$$\sum_{M=1}^{N(|\boldsymbol{\beta}_j|)}\tilde{\chi}_{Mn}$$

interacting with the charge distribution of the remaining electrons of the system is diagonalized, leading directly to a set of coefficients, $U_i(|\boldsymbol{\beta}_j|)$, corresponding to the ith eigenvalue.

Let

$$T_a\equiv-(\hbar^2/2m)\nabla_a^2, \tag{7}$$

$$U_{Ia}\equiv-Z_I|e|^2/|\mathbf{R}_I-\mathbf{r}_a|, \tag{8}$$

$$C_{Ia}\equiv|e|^2\sum_{i=1}^{Z_I}\int\frac{|\varphi_{Ii}(i)|^2}{|\mathbf{r}_i-\mathbf{r}_a|}d\tau_i, \tag{9}$$

$$X_{Ia}(Kk,\ Jj)$$

$$\equiv-|e|^2\sum_{i=1}^{Z_I}\int\frac{\varphi_{Ii}(a)\varphi_{Kk}{}^*(a)\varphi_{Ii}{}^*(i)\varphi_{Jj}(i)\,d\tau_i}{\varphi_{Kk}{}^*(a)\varphi_{Jj}(a)\,|\mathbf{r}_i-\mathbf{r}_a|}. \tag{10}$$

Since $X_{Ia}(Kk,\ Jj)$ is a nonlocal potential which is not defined unless $\varphi_{Kk}{}^*$ and φ_{Jj} are first defined, we can display the crystal Hamiltonian in general only by adopting the symbol X_{Ia} to mean that potential which is defined only in terms of matrix elements such that

$$\int\varphi_{Kk}{}^*(a)X_{Ia}\varphi_{Jj}(a)d\tau_a=\int\varphi_{Kk}{}^*(a)X_{Ia}(Kk,\ Jj)\varphi_{Jj}(a)\,d\tau_a. \tag{11}$$

Thus, the crystal Hamiltonian for the ath (excited) electron can be written in the form

$$\mathcal{H}(a)=T_a+U_{Aa}+C_{Aa}+X_{Aa}+\sum_{I(\neq A)}[U_{Ia}+C_{Ia}+X_{Ia}]. \tag{12}$$

The matrix equation to be solved is then

$$\boldsymbol{\mathcal{H}}\tilde{\mathbf{X}}=\mathbf{S}\tilde{\mathbf{X}}\epsilon, \tag{13}$$

where

$$\mathcal{H}_{ij}=\sum_{M=1}^{N(|\boldsymbol{\beta}_i|)}\sum_{N=1}^{N(|\boldsymbol{\beta}_j|)}\int\tilde{\chi}_{Mn}\mathcal{H}(a)\tilde{\chi}_{Nn}d\tau_a \tag{14}$$

and

$$S_{ij}=\sum_{M=1}^{N(|\boldsymbol{\beta}_i|)}\sum_{N=1}^{N(|\boldsymbol{\beta}_j|)}\int\tilde{\chi}_{Mn}\tilde{\chi}_{Nn}d\tau_a. \tag{15}$$

(The functions $\tilde{\chi}_{Mn}$ are real so that $\tilde{\chi}_{MN}{}^*=\tilde{\chi}_{Mn}$.)

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[9] See, for example, p. 1037 of J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954).

[10] G. Wannier, Phys. Rev. **52**, 191 (1937).

[11] Also see R. S. Knox, Solid State Phys. Suppl. **5**, Sec. 3e (1963).

Because the functions $\tilde{\chi}_{Mn}$ are rather complicated, the expressions for the elements are lengthy. Rather than reproduce here the equations and approximations used in our previous work, the reader is referred to that earlier paper[7] (see Appendix I). Perhaps the most serious approximation required is the Mulliken approximation to certain large three-center integrals. This approximation is expressible in the form

$$\bar{\varphi}_{Mn}\bar{\varphi}_{Nn}\approx\tfrac{1}{2}\langle\overline{Mn}\mid\overline{Nn}\rangle\{\bar{\varphi}_{Nn}{}^2+\bar{\varphi}_{Mn}{}^2\}. \tag{16}$$

The calculation, when carried out in the supermolecule approximation, is for a small part of the crystal consisting of one argon atom and 135 surrounding neon atoms. The inclusion of this number of atoms assures nearly complete convergence of the calculated energy terms and is expected to be sufficiently large for the description of all but long-range effects. The wavefunctions used are listed in Appendix II. It should be mentioned that different choices of the ground-state neon SCF function can lead to fairly large differences in the individual energy terms, but to lesser differences in the complete matrix elements due to the large cancellation of terms typical of these calculations.[12]

The values of the resulting matrix elements are reported in Sec. III.

B. Lattice Configurations

In the static-lattice approximation it is necessary to obtain an accurate estimate of the equilibrium nuclear configuration of the lattice. This information is generally available for pure crystalline solids from x-ray or neutron-diffraction studies. For the case of an impurity atom which is larger or smaller than the host crystal atoms, the local distortion surrounding the impurity must be estimated theoretically since, in general, no experimental data are available.

Gold[1] has studied the ground-state configuration of the Ar–Ne system by using the usual combining rules for the Lennard-Jones[9] potential between an argon atom and the surrounding neon atoms, therefrom computing the configuration that leads to the minimum energy. We have made a similar calculation by estimating the pressure required to form a bubble in crystalline neon: We use the macroscopic compressibility of solid neon and relate this to the gradient of the Ar–Ne intermolecular pair potential. The calculation leads to the same results as obtained by Gold. The resultant nuclear configuration is: $|\beta_1|=6.3a_0(a_0=\text{Bohr radii})$, $|\beta_2|=8.3a_0$, and $|\beta_3|=10.2\ a_0$. For pure neon $|\beta_1|=5.82\ a_0$ and for pure argon $|\beta_1|=7.10\ a_0$, so that the estimated distortion is about as expected. The equilibrium nuclear configuration of the lattice will undoubtedly be different in the excited state, but that is not pertinent in this calculation since we consider only the state reached by a vertical excitation (no change of nuclear position during the time of transition). The eigenvalues of the matrix diagonalization are sensitive to the magnitudes of the shell separations, but not so drastically as one might at first think (see Ref. 6). Since the primary purpose of this calculation is to test the effect of increased flexibility in the representation of the excited electron orbital and is not an attempt to predict all of the details of the absorption spectrum of the argon atom, we do not vary the nuclear configuration in order to vary the expected transition energies.

III. DISCUSSION OF NUMERICAL RESULTS

In Tables I, II, and III are displayed the calculated matrix elements. The various terms I_A, I_B, $\cdots$, are defined in our previous paper[7] and Appendix I. It should be noted that the entries are, in all cases, just $H_{ij}/N(\beta_j)$,[13] since the symmetry of the system makes valid the identification

$$\begin{aligned} O_{ij}&=\sum_{N=1}^{N(\beta i)}\sum_{M=1}^{N(\beta j)}(\tilde{\chi}_{Mn}\mid\hat{O}\mid\tilde{\chi}_{Nn}) \\ &=N(\beta_i)\sum_{M=1}^{N(\beta j)}(\tilde{\chi}_{Mn}\mid\hat{O}\mid\tilde{\chi}_{Nn}) \end{aligned} \tag{17}$$

for any operator $\hat{O}$, that has the spherical symmetry of the system.

The value of N and the range of M for each element is also given in the Tables I–V so as to assist in the interpretation of the figures displayed. The numbering system is as follows: $N=1$ refers to the central or Ath atom, the argon in this case; $N=2$ through $N=13$ refer to the first shell of neon atoms; $N=14$ to $N=19$ and $N=20$ to $N=43$ refer, respectively, to the second and third shells of neon atoms.

A brief comparison of the entries in Tables I, II, and III with the corresponding matrix elements for the case of pure Ne reveals striking similarities. The diagonal element H_{11} in the case of pure neon is about 1 eV lower in energy than for the case of the argon–neon system. This difference reflects directly the 1-eV

TABLE I. H_{11} terms (in electron volts).

I_A	I_B	I_C	I_D	I_E	H_{11}
−4.415	7.391	−5.249	0.574	$\cdots$	1.699

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[12] Comparison of H_{11} with the value calculated by Gold (see Ref. 2) shows that the energy of a Schmidt-orthogonalized $4s$ orbital in the distorted neon lattice, as calculated herein, is about 2.5 eV lower than that calculated by Gold. This disagreement could arise from the use of different neon SCF functions or from a numerical error. Gold has indicated in a private communication that there may be numerical errors in his work because the values of integrals were taken over from the earlier symmetrically orthogonalized calculation (see Ref. 1) to the Schmidt orthogonalized calculation (Ref. 2). The very complicated algebra connecting these two methods provides ample opportunity for errors.

[13] We use the symbol $N(\beta_i)$ to mean $N(|\beta_i|)$ hereafter.

TABLE II. H_{1j} terms (in electron volts).

J_A	J_B	J_C	$J_D{}^{+\,a}$	J_E	J_F	J_G	$\Sigma_I J_I$	H_{ij}
−27.068	34.647	2.983	−26.855	2.519	···	···	−13.774 =	$H_{12}{}^{b}$
−9.256	15.179	0.606	−9.728	1.110	···	···	−2.089 =	$H_{13}{}^{b}$
−23.474	42.882	0.825	−24.147	2.982	···	···	−0.932 =	$H_{14}{}^{b}$

[a] + denotes three-center term in all tables.

[b] For the H_{1j} elements we display the full value of the matrix element and not $H_{1j}/N(\beta_j)$.

difference between the energies of the SCF atomic orbitals for 4*s* (argon) and 3*s* (neon).[14] It is also interesting to note that atomic crowding results in little energy change (i.e., the value of H_{11} is little effected), the reason being that the orthogonality energy[15] of the argon–neon system is increased relative to pure neon, but the penetration energy[16] is favorably decreased, leading to effective cancellation of the separate terms. In both cases the element H_{11} is about 2 eV higher in energy than the SCF orbital energy.

In carrying out the diagonalization in a straightforward manner we encountered a difficulty in that the set of functions defining the 4×4 energy matrix is, accidentally, nearly linearly dependent. The near-linear dependence, coupled with the errors arising from the approximations inherent in the analysis, leads to an impossible result, i.e., the implication that $(\psi_{Aa}\,|\,\psi_{Aa})<0$. It is easy to find that member of the original basis set which is accidentally linearly dependent on the others; this function was then discarded. It was found that elimination of the functions $\tilde{\chi}_{Nn}$ on the second shell (located $8.3a_0$ from the Ar atom) leads to the lowest energy of the three possible 3×3 energy matrices, and this energy is about 0.02 eV higher than the corresponding energy from the 4×4 energy matrix (i.e., disregarding the one impossible root which arises from a near singularity in the overlap matrix). Table VI displays the lowest eigenvalue of the energy matrix, as well as the corresponding eigenvector.

Undoubtedly the most serious numerical uncertainties in the work reported herein arise from the use of the Mulliken approximation to evaluate three-center terms. The Mulliken approximation has been found to give remarkably accurate results for certain advantageous cases, and the configuration with strongly overlapping *s* functions is believed to be one such advantageous case (see Ref. 7, Table XVII). To test the sensitivity of our calculation to the values assigned to the three-center terms, eigenvalues were calculated for energy matrices in which the three-center terms were ± 10% of those reported in Tables II and V. The lowest eigenvalues for these two cases differed by only 0.05 eV from each other, roughly symmetrically about the value displayed in Table VI. It would appear that errors in the three-center terms lead to less uncertainty in our final result than the neglected change of the van der Waals energy.

IV. DISCUSSION OF THE CHARGE-TRANSFER WAVEFUNCTION

In the present work, as well as in our previous study of crystalline neon, it has been found that the addition of basis functions located at distances $|\beta_i|$ from the central hole leads to significant lowering of the orbital energy of the excited electron. It is, therefore, desirable to analyze the supermolecule wavefunction used in more detail.

We observed in our study of crystalline neon that the greatest improvement in the orbital energy of the excited electron came about when the atoms of the first shell were nearly completely surrounded by other atoms in the supermolecule. The increase of the energy of the 3*s* SCF function (for the ^1P state of Ne) arises mostly from interaction with the first shell of surrounding atoms, and it is therefore not surprising that "added flexibility" in this region of the crystal lowers the energy. In the case of the argon–neon mixed solid, the second shell of the supermolecule is important

TABLE III. H_{ij} values (in electron volts, see Tables IV, V).

$\sum_I K_I$	$\sum_I L_I$	Sum	Element $=H_{ij}/N(\beta_i)$	N	Range of M
0.578	8.483	9.061	$H_{22}/12$	2	3–13
1.330	2.877	4.207	$H_{33}/6$	14	15–19
1.925	10.104	12.029	$H_{44}/24$	20	21–43
···	3.538	3.538	$H_{23}/12$	2	14–19
···	12.723	12.723	$H_{24}/12$	2	20–43
···	13.654	13.654	$H_{34}/6$	14	20–43

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[14] For argon see R. Knox. Phys. Rev. **110**, 375 (1958); for neon see A. Gold and R. Knox, *ibid.* **113**, 834 (1959).

[15] Orthogonality energy is herein defined as the increase in energy due to the nodes introduced by orthogonalization of the excited state to the orbitals of the surrounding Ne atoms: It is denoted I_B and I_D in Table I, where I_B and I_D are defined in Appendix I, (A3) and (A5).

[16] Penetration energy is herein defined as the net energy of the test electron interacting with the neutral atoms and is always negative in the cases under consideration. In Table I, it is denoted by I_C, defined by (A4).

TABLE IV. H_{ii} terms ($i\neq 1$, in electron volts).

K_A	K_B	K_C	K_D	K_E	K_F	K_G	$\Sigma_I K_I$	N	H_{ii}[a]
2.854	6.811	−5.544	−3.874	0.331	···	···	0.578	2	H_{22}
2.803	6.141	−3.704	−4.251	0.341	···	···	1.330	14	H_{33}
2.806	6.310	−2.991	−4.520	0.320	···	···	1.925	20	H_{44}

[a] Denotes matrix element of which the terms K_I are a part.

because of the atomic crowding, and it is found that the energy lowering arising from the inclusion of the same number of charge-transfer states in the basis set is smaller than in pure crystalline neon. Presumably, a larger charge-transfer set would be needed to reach convergence for the Ar–Ne case.

It is of interest to study the expectation value of various parts of the crystal Hamiltonian with respect to the function ψ_{Aa}. For convenience we examine the 1,1 element energy terms, where $\langle\overline{Aa}\,|$ should now be taken to be ψ_{Aa} instead of $\bar{\varphi}_{Aa}$. There are three contributions to the orbital energy: (1) interaction of the electron with the argon hole, given[17] by I_A (see Appendix I for these terms), (2) orthogonalization energy given by I_B+I_D, and (3) penetration energy, given by I_C. These energies are displayed in Table VII. It is important to note that the lowering of the energy effected by the inclusion of CT states is mainly concentrated in one term, the orthogonalization energy. Also, we observe that the attractive contributions to $\langle\mathcal{H}(a)\rangle$ have decreased in magnitude. Now, orthogonalization energy is an artificial construct in the sense that it describes the departure of the variation-function orbital from the true crystal orbital (which would have zero orthogonalization energy). Thus, what we have really shown in this work (and perhaps also in our study of crystalline Ne) is how *bad* the orthogonalized SCF function is as a representation of the lowest crystal excited state.

Examination of the charge density of the orthogonalized 4*s* SCF function and the full charge-transfer function shows that the difference in charge density is small almost everywhere (see Ref. 6 for example).

In order to analyze further the above observation, a rough comparison was made of the expectation value of $\langle\mathbf{r}^2\rangle$[18] in the basis of the unmixed SCF function and the charge-transfer function. Contrary to expectations based on the presence of functions with $|\beta_i|\neq 0$, it is found that $\langle\mathbf{r}^2\rangle$ is almost the same for the CT function and for the SCF 4*s* argon orbital (about $31a_0^2$). Thus, it would seem that our basis function (which was chosen because it seemed physically reasonable and resembled the Wannier approach) has functioned primarily to repair a very bad starting function for the lowest rare-gas crystal excited state, namely, the SCF isolated-atom wavefunction. In the next section we discuss what we now believe to be a more reasonable approach to this problem along with some criteria for choosing starting functions for the study of bound excited states in molecular crystals.

TABLE V. Terms for H_{ij} ($i,j\neq 1$, in electron volts).

L_A	L_B	L_C	L_D^+	L_E	L_F	L_G	L_H^+	$\Sigma_I L_I$	N	Range of M	H_{ij}[a]
8.294	26.087	0.088	−10.812	0.937	···	···	−16.111	8.483	2	3–13	H_{22}
1.122	4.098	0.087	−1.415	0.218	···	···	−1.233	2.877	14	15–19	H_{33}
6.203	18.287	0.898	−9.635	0.963	···	···	−6.612	10.104	20	21–43	H_{44}
4.012	10.297	0.682	−5.413	0.507	···	···	−6.547	3.538	2	14–19	H_{23}
10.808	30.037	1.700	−15.157	1.592	···	···	−16.257	12.723	2	20–43	H_{24}
9.243	26.294	1.465	−13.760	1.446	···	···	−11.034	13.654	14	20–43	H_{34}

[a] Denotes the matrix element of which the terms L_I are a part.

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[17] In the calculations reported herein the values of (1) for the charge-transfer functions were taken as the net difference of the repulsion due to the neutral neon and the attraction of the $3p^5$ argon hole.

[18] The coordinate system has the point $r=0$ as the argon atom for this calculation.

V. DISCUSSION OF BOUND EXCITED-STATE CALCULATIONS

Let us first state our objective: We seek to obtain the best single-product wavefunction for the molecular solid. This is, by definition, the SCF function. Although SCF functions are now being computed for atoms and diatomic molecules, no such calculations for solids seem presently feasible. For this reason we must lower our expectations and attempt only to approach the best single-product wavefunction. It should be pointed out immediately that it is by no means obvious that the single-product restriction will lead to the best crystal wavefunction. For pure crystals of $N_1 \times N_2 \times N_3$ atoms, the most general Frenkel wavefunction for the excited state is of the form

$$\phi_e{}^K = N \sum_{J=1}^{N_1 \times N_2 \times N_3} \exp(i\mathbf{K} \cdot \mathbf{R}_J) \sum_i \alpha_i \mathcal{A} \bar{\psi}_{Jj} \sum_{Kk(\neq Jj)} \varphi_{Kk}{}^i, \quad (18)$$

where N is the normalization constant, $\bar{\psi}_{Ji}$ the ith excited orbital on the Jth nuclear site, α_i the weight of that state, and the $\varphi_{Kk}{}^i$ are the lower orbitals belonging to the SCF Hamiltonian of the ith excited state. Exchange interactions between configurations are often very important in such a crystal state, and the best choices for single-product functions might not lead to the best basis states for the full configuration-interaction wavefunction.[19]

TABLE VI. ϵ_1 and coefficients.

ϵ_1	$U_1(\lvert \mathbf{0} \rvert)$	$U_1(\lvert \beta_1 \rvert)$	$U(\lvert \beta_3 \rvert)$
−2.26	0.8397	0.0586	−0.0508

TABLE VII. Comparison of charge-transfer set and 4s argon SCF function energy terms, in electron volts.

	$4s^{\mathrm{SCF}}$	Charge transfer	Difference
Interaction with argon hole	−4.4	−3.5	+0.9
Penetration energy	−5.3	−4.7	+0.6
Orthogonalization energy	8.0	6.0	−2.0
Net energy	−1.7	−2.2	−0.5

Consider now how to best choose basis functions for $\bar{\psi}_{Ji}$, by a method other than that of picking a set of functions on purely intuitive grounds (a method which has been very useful when orthogonality corrections are small followed by a full variational calculation. We focus attention on the application of pseudopotential or pseudo-Hamiltonian techniques. This approach was first used by Phillips and Kleinman,[20] and later discussed in more detail by Cohen and Heine,[21] and by Austin, Heine, and Sham (AHS),[22] who have also discussed the general properties of pseudopotentials. AHS point out that the pseudopotential can be written in the general form

$$V_R \mid \phi \rangle = \sum_{t=1}^{N} \langle F_t \mid \phi \rangle \mid \phi_t \rangle, \quad (19)$$

where we now use the bra and ket notation of Dirac.[23] In (19) V_R is a nonlocal potential[21,22] which projects the $\mid \phi_t \rangle$ out of the space of the "smooth" function $\mid \phi \rangle$. The treatment assumes that the lower N electronic states of a particular Hamiltonian are known. The pseudo-Hamiltonian of the system is now

$$\mathcal{H}_p = \mathcal{H} + V_R. \quad (20)$$

The pseudo-Hamiltonian $\mathcal{H}_p$ is particularly useful in finding an advantageous function $\mid \phi \rangle$ or set of $\mid \phi_i \rangle$ to represent the smooth part of an excited-state orbital. If $\mathcal{H}_p$ is to be used with some arbitrary function $\mid \phi \rangle$, it is necessary that $\mathcal{H}_p$ be defined such that the arbitrary function $\mid \phi \rangle$ will converge to the lowest excited state and not to some lower energy function, $\mid \phi_t \rangle$. Such a condition is satisfied if the "energy" corresponding to the functions $\mid \phi_t \rangle$ (the core functions) when operated on by the Hamiltonian $\mathcal{H}_p$ is large. Then the lowest energy corresponding to the variational function will be roughly related to the energy of an excited state, or at least that function with the lowest algebraic value of

$$\tilde{E}_p = \langle \phi \mid \mathcal{H}_p \mid \phi \rangle / \langle \phi \mid \phi \rangle \quad (21)$$

will correspond to the best fit to the "smooth part" of $\mid \phi_{N+1} \rangle$, the true $(N+1)$th state.

Consider now the calculation of the matrix elements of a very poor function $\mid \phi \rangle$, say

$$\mid \phi_n \rangle = \sum_{t=1}^{N} \beta_t \mid \phi_t \rangle, \quad (22)$$

which is as different from $\mid \phi_{N+1} \rangle$ as possible. The secular equation for $\mid \phi_n \rangle$ is

$$\det \mid (E_t - \tilde{E}) \delta_{t,t'} + \langle F_{t'} \mid \phi_t \rangle \mid = 0. \quad (23)$$

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[19] See, for example, R. S. Knox, J. Phys. Chem. Solids **9**, 238, 265 (1959) for application of the Frenkel exciton formalism to solid argon.

[20] J. C. Phillips and L. Kleinman, Phys. Rev. **116**, 287 (1959); **118**, 1153 (1960).

[21] M. H. Cohen and V. Heine, Phys. Rev. **122**, 1821 (1961).

[22] B. J. Austin, V. Heine and L. J. Sham, Phys. Rev. **127**, 276 (1962).

[23] P. A. M. Dirac, *The Principles of Quantum Mechanics* (Oxford University Press, London, 1958), 4th ed., see especially Sec. 20.

Let $\langle F_{t'} |$ be such that the off-diagonal terms of (23) are small. Then the perturbation approximation to the tth root is

$$\tilde{E}_t = E_t + \langle \phi_t | F_t \rangle - \sum_{t'=1(\neq t)}^{N} \frac{| \langle \phi_t | F_{t'} \rangle |^2}{(E_{t'} - E_t)}. \quad (24)$$

We wish $\tilde{E}_t$ to be larger than E_{N+1}, and at least greater than zero. As pointed out by AHS, if

$$\langle F_t | = -\langle \phi_t | V, \quad (25)$$

where V is the true potential, then

$$\tilde{E}_t = E_t - \langle \phi_t | V | \phi_t \rangle + \text{perturbation terms}. \quad (26)$$

Ignoring the perturbation terms for the present and using the order of magnitude result that

$$\langle \phi_t | V | \phi_t \rangle \approx 2E_t, \quad (27)$$

then

$$\tilde{E}_t \approx -E_t, \quad (28)$$

which is far into the continuum. If

$$\langle F_t | = -\langle \phi_t | \mathcal{H} = -E_t \langle \phi_t |, \quad (29)$$

then

$$\tilde{E}_t = 0, \quad (30)$$

so that the choice of (29) for $\langle F_t |$ is satisfactory so long as we deal with bound states. The choice of (29) for $\langle F_t' |$ is particularly simple to use, and is closely related to the Phillips-Kleinman[20,22] function

$$\langle F_t | = (E_{N+1} - E_t) \langle \phi_t |. \quad (31)$$

Our problem is now defined: We seek that set of basis functions which gives, with $\mathcal{H}_p'$, the lowest energy, and where

$$\mathcal{H}_p' = \mathcal{H} - \sum_{t=1}^{N} | \phi_t \rangle \langle \phi_t | \mathcal{H}$$

$$= \mathcal{H} - \sum_{t=1}^{N} E_t | \phi_t \rangle \langle \phi_t |. \quad (32)$$

The reader should note that (32) is not much easier to use than the form proposed by Phillips-Kleinman. However, (32) has advantages when used on a single function to determine the best value of a parameter, such as an orbital exponent or quantum number. The latter part of $\mathcal{H}_p$ is quite easy to compute and the matrix of this part of $\mathcal{H}_p$ may be easily constructed. Given a "family" of trial functions $| \phi_n \rangle$, each of which gives reasonably low values of $\tilde{E}_p'$, it is advantageous to find that linear combination which minimizes the operator

$$\mathcal{R} = -\sum_{t=1}^{N} E_t | \phi_t \rangle \langle \phi_t |. \quad (33)$$

This calculation aids in the choice of the smallest possible set of functions $| \phi_n \rangle$ to be used in the full variational treatment. For example, when the three-shell charge-transfer set of the Ar:Ne supermolecule function is used to minimize the operator $\mathcal{R}$, the lowest eigenvalue is 4.4116 eV; when the four-shell set is used ($| \beta_i | = 0$, 6.3, 8.3, $10.2a_0$ with the $8.3a_0$ shell missing for the former calculation), the lowest eigenvalue is 4.4048 eV. This calculation confirms that the shell at $8.3a_0$ is not required for a successful variational treatment, and in fact complicates matters by introducing near-linear dependency. We should point out that it is very dangerous to use the minimization of $\mathcal{R}$ too extensively without also checking the expectation values of the functions with $\mathcal{H}$. In the case of the charge-transfer set, the expectation values of the functions at $\beta \neq \mathbf{0}$ with $\mathcal{H}$ are nearly the same, so that the use of $\mathcal{R}$ yields meaningful results.[24]

The value of $\tilde{E}_p'$ for the SCF 4s argon function, which is the leading term of Eq. (4), is of considerable interest. By way of comparison, the values of $\tilde{E}_p'$ for a set of hydrogenic 1s functions were also computed: These are defined in terms of a parametric dielectric constant by

$$1s(\epsilon) = (4\pi)^{-\frac{1}{2}} 2\epsilon^{-\frac{3}{2}} \exp\{-r/\epsilon\}. \quad (34)$$

The results of these computations are displayed in Table VIII. It is seen that the $\epsilon = 3$ hydrogenic function leads to the lowest value of $\tilde{E}_p'$, indicating that it might be a far more appropriate starting function in the representation of the ${}^1P$, ${}^3P$ crystal states than is the SCF 4s function. The "core functions" were taken to be those of the $(1s)^2(2s)^2(3s)^2(2p)^6(3p)^5 4s({}^1P)$ state of argon and the $(1s)^2(2s)^2(3p)^6({}^1S)$ state of

TABLE VIII. Values of $\tilde{E}_p'$ for hydrogenic set and SCF 4s function, in electron volts.

Function	$\langle \mathcal{H} \rangle$	$\langle R_A \rangle$[a]	$\langle R_I \rangle$[b]	E_p'
1s (3)	−25.202	17.369	3.990	−3.842
1s (5)	−13.414	5.438	4.143	−3.833
1s (7)	−9.000	2.370	5.082	−1.548
1s (9)	−6.559[c]	0.973	3.962[c]	−1.624
4s	−7.559[d]	0.0	6.490[d]	−1.833[d]

[a] $R_A = \sum_{Aj} -E_{Aj} | \phi_{Aj} \rangle \langle \phi_{Aj} |$.

[b] $R_I = \sum_{Ii} -E_{Ii} | \phi_{Ii} \rangle \langle \phi_{Ii} |$.

[c] There is doubt if this value is correct as convergence of the crystal terms may not have occurred. Values were taken for neons out to 10.2 a_0, while this function has its maximum at 9 a_0.

[d] These values are different than reported in Table I as we are not using the Schmidt orthogonalized 4s, so that the normalization constant is different.

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[24] We note that the final value of $\langle \mathcal{R} \rangle$ is about 5.1 eV for the full variational function (corrected for normalization differences) so that the remainder of $\mathcal{H}_p$ prevents the minimum value of $\langle \mathcal{R} \rangle$ from being reached.

neon. A $1s(\epsilon)$ function is quite different from the SCF $4s$ function, and it is therefore to be expected that the energy of the argon atom in the $(1s)^2(2s)^2(3s)^2(2p)^6(3p)^5 1s(\epsilon)(^1P)$ state will be different from the SCF ^1P state. Using the SCF program recently discussed by Roothaan and Bagas,[25] the energy of the atom using the hydrogenic function was determined for all the values of ϵ considered in the next section (3, 5, 7, 9), as well as $\epsilon=1$, 2 for comparison (see Table IX).[26] It is seen that the $\epsilon=3$ and 5 basis functions give total atom energies only about 0.3 eV higher than that obtained from the SCF $4s$ function. This energy increase is more than offset by the interaction with the rest of the crystal Hamiltonian, expecially the $\mathcal{R}$ operator (see Table VIII for example).

VI. PASSAGE TO A MODEL HAMILTONIAN

One of the intriguing aspects of the study of the electronic states of solids has been the success of some very simple models. The experiments of Baldini[27] on solid rare gases present one of these cases. In the spectrum of solid Ar, Kr, and Xe, Baldini has observed a series of hydrogenic lines, relatively sharp and presumably arising from transitions between bound states. These lines were most clearly seen in the spectra of annealed Xe crystals, in which the three absorption peaks at 8.36, 9.07, and 9.19 eV could be fitted to the series

$$h\nu_n = E_{\text{gap}} - G/n^2 \tag{35}$$

with fair accuracy. Fewer sharp lines appear in the Kr and Ar spectra, and the assignment of these peaks to a hydrogenic series seems to be less certain. We have discussed the possibility of using charge-transfer states farther removed from the hole and eventually reaching values of $\mathfrak{B}$ large enough to make direct comparison with Wannier's original treatment. In this section we discuss the possibility that the nature of a particular solid may make valid the use of a simple model Hamiltonian.

TABLE IX. SCF results for ^1P argon atom using a minimal basis set, in atomic units.

Function	Excited orbital energy	Total energy
$1s$ (1)	+0.16495	−525.13786
$1s$ (2)	−0.07582	−525.37548
$1s$ (3)	−0.11787	−525.41671
$1s$ (5)	−0.11938	−525.41751
$1s$ (7)	−0.10362	−525.40149
$1s$ (9)	−0.08889	−525.38667
$4s$	−0.13158	−525.42986

Cohen and Heine[21] have discussed the use of the pseudopotential as a method of testing model Hamiltonians. These investigators set

$$\langle F_t | = -\langle \phi_t | (V - V_M), \tag{36}$$

whereupon

$$\begin{aligned} \mathcal{H}_p &= \mathcal{H} - \sum_{t=1}^{N} |\phi_t\rangle\langle\phi_t| (V - V_M) \\ &= \mathcal{H}_M + (V - V_M) - \sum_{t=1}^{N} |\phi_t\rangle\langle\phi_t| (V - V_M) \end{aligned} \tag{37}$$

with

$$\mathcal{H}_M = T_a + V_M. \tag{38}$$

For any choice of V_M it is necessary that $\tilde{E}_t$ remain greater than zero. If the set $|\phi_t\rangle$ is complete, then $\mathcal{H}_p = \mathcal{H}_M$ for any arbitrary V_M including zero, so $\mathcal{H}_p = T_a$ and the conduction band results.

A perhaps more useful observation is that for a proper choice of V_M, the quantity $V - V_M$ can be expanded in the set $|\phi_t\rangle$. As an example let us consider a hydrogen atom embedded in a rare-gas matrix. In that case the SCF potential V would be taken to be

$$V = -|\mathbf{R}_A - \mathbf{r}|^{-1} + \sum_{I(\neq A)} [U_{Ia} + C_{Ia} + X_{Ia}]. \tag{39}$$

If

$$V_M = -|\mathbf{R}_A - \mathbf{r}|^{-1}, \tag{40}$$

then

$$\begin{aligned} \mathcal{H}_p = \mathcal{H}_{\text{hydrogen}} + \{ &\sum_{I(\neq A)} [U_{Ia} + C_{Ia} + X_{Ia}] \\ &- \sum_J \sum_{Ii} |\phi_{Ii}\rangle\langle\phi_{Ii}| [U_{Ja} + C_{Ja} + X_{Ja}] \}. \end{aligned} \tag{41}$$

If the set of $|\phi_{Ii}\rangle$ at each Ith nucleus is fairly large, it is quite likely that the bracketed part of Eq. (41) will almost cancel. This cancellation occurs because the potential $[U_{Ia} + C_{Ia} + X_{Ia}]$ and the set $\sum_i |\phi_{Ii}\rangle\langle\phi_{Ii}|$ occupy the same region of real space and drop off to zero at about the same rate. On the basis of these considerations alone one would predict that the spectrum of a hydrogen atom in a xenon matrix would be less shifted from the free-atom spectrum than in a neon or argon matrix. This observation is rather crude, of course, and neglects the effects of polarization of the medium by a charge distribution, different crystal strains due to mismatched atomic diameters, etc.

The preceding discussion has emphasized the role of the set $|\phi_t\rangle$ in the use of a model Hamiltonian. This is not really correct, of course, as what is of real interest is the value of

$$\Delta = \langle\phi| V - V_M |\phi\rangle - \sum_{t=1}^{N} \langle\phi|\phi_t\rangle\langle\phi_t| V - V_M |\phi\rangle, \tag{42}$$

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[25] C. C. J. Roothaan and P. S. Bagas, *Methods in Computational Physics* (Academic Press Inc., New York, 1963), Vol. 2, pp. 47–94.

[26] The resulting SCF $1s(E)$ orbital is orthogonal to the argon core.

[27] G. Baldini, Phys. Rev. **128**, 1562 (1962).

TABLE X. The value of Δ for hydrogenic set, in electron volts.

Function	Δ_A[a]	Δ_I[b]	Δ
1*s* (3)	−5.177	1.641	−3.536
1*s* (5)	−3.620	0.055	−3.565
1*s* (7)	−3.471	1.531	−1.940
1*s* (9)	−2.986	1.193[c]	−1.793

[a] Δ_A is the value of $V-V_M$ due to the Ath atom and is the value of

$$-[(\epsilon-1)/\epsilon](|\mathbf{R}_A-\mathbf{r}|)^{-1}+\sum_{Aj}[(\epsilon-1)/\epsilon]|\phi_{Aj}\rangle\langle\phi_{Aj}||\mathbf{R}_A-\mathbf{r}|^{-1}$$
$$+[U_{Aa}^0+C_{Aa}^0+X_{Aa}^0]-\sum_{Aj}|\phi_{A_j}\rangle\langle\phi_{A_j}|[U_{Aa}^0+C_{Aa}^0+X_{Aa}^0].$$

[b] Δ_I is the part of Δ due to the remaining neons and is the value of

$$\sum_I\{[U_{Ia}+C_{Ia}+X_{Ia}]-\sum_i|\phi_{Ii}\rangle\langle\phi_{Ii}|[U_{Ia}+C_{Ia}+X_{Ia}-(1/\epsilon|\mathbf{R}_A-\mathbf{r}|)]\}.$$

[c] This value may be incorrect, see Table VIII, Footnote c.

where $|\phi\rangle$ is again an arbitrary smooth function. The function $|\phi\rangle$ may contain adjustable parameters to make (42) vanish as completely as possible within the set of $|\phi_t\rangle$. If $|\phi(\alpha)\rangle$ represents a function with an adjustable set of parameters α, we may choose $|\phi(\alpha)\rangle$ to be an eigenfunction of a particular model Hamiltonian $\mathcal{H}_M(\alpha)$. We now seek to find the best model Hamiltonian by evaluating Δ for a series of values of α. Even if it is possible to find an α such that $\Delta=0$, it may be that the resulting $|\phi(\alpha)\rangle$ leads to a higher value of $\tilde{E}_p'$ [Eqs. (21) and (32)] than some other function $|\phi\rangle$ which has no relation to $\mathcal{H}_M(\alpha)$. In such a situation, we discard $\mathcal{H}_M(\alpha)$ as having no physical meaning for the case under study. The procedure cited is tedious, but it is simplier than application of the full variational treatment and may lead to considerably more physical insight.

We should again stress that care in the choice of V_M is necessary to fulfill the small mixing criterion and large $\tilde{E}_t$ of Eq. (24). If there is the possibility of strong mixing of part of the set $|\phi_t\rangle$, then $|\phi(\alpha)\rangle$ should be chosen so as to have fairly small overlap with that part of the set $|\phi_t\rangle$, in order to prevent convergence to a lower state.

Returning to the study of Ar:Ne, consider again the hydrogenic Hamiltonian

$$\mathcal{H}_H(\epsilon)=T_a-(1/\epsilon|\mathbf{R}_A-\mathbf{r}|), \qquad (43)$$

which gives

$$V-V_M=-[(\epsilon-1)/\epsilon](1/|\mathbf{R}_A-\mathbf{r}|)$$
$$+[U_{Aa}^0+C_{Aa}^0+X_{Aa}^0]+\sum_{I(\neq A)}[U_{Ia}+C_{Ia}+X_{Ia}]. \qquad (44)$$

The symbol $[C_{Aa}^0+X_{Aa}^0+U_{Aa}^0]$ represents the "local" part of the excited argon atom potential and has the limiting value $-17/|\mathbf{R}_A-\mathbf{r}|$ as $|\mathbf{R}_A-\mathbf{r}|\rightarrow 0$. When the set

$$|\phi(\epsilon)\rangle=(4\pi)^{-\frac{1}{2}}2\epsilon^{-\frac{3}{2}}\exp\{-r/\epsilon\}\equiv|1s(\epsilon)\rangle \qquad (45)$$

is used for the argon neon case, it is found that the cancellation is best for large values of ϵ (see Table X), but the total energies of these states are higher than the energies of the states corresponding to lower values of ϵ (3 or 5, for example). These considerations suggest the use of $|1s(3)\rangle$ in an SCF calculation for the ^1P state of argon discussed in the last section.

We conclude, therefore, that hydrogenic lines might not be observed in the argon–neon case even if it were possible to do the experiment (the absorption shoulder of neon makes any structure of the argon spectrum impossible to observe[5]).

Is there any way to obtain a reasonable estimate of the best $\mathcal{H}_H(\epsilon)$ given the set of $|\phi_t\rangle$? If the set of $|\phi_{Aj}\rangle$ (the excited-atom lower orbitals) is reasonably complete, it is expected that the best choice of ϵ would be that which puts the charge density of $|1s(\epsilon)\rangle$ in the region of the $|\phi_{Aj}\rangle$ because the most important term in $V-V_M$ is usually $(1-1/\epsilon)\ |\mathbf{R}_A-\mathbf{r}|^{-1}$. Then, if the interaction of $|1s(\epsilon)\rangle$ with this potential is mostly in the region of the $|\phi_{Aj}\rangle$, the cancellation of

$$[(\epsilon-1)/\epsilon]\{\langle 1s(\epsilon)||\mathbf{R}_A-\mathbf{r}|^{-1}|1s(\epsilon)\rangle$$
$$-\sum_{Aj}\langle 1s(\epsilon)|\phi_{Aj}\rangle\langle\phi_{Aj}||\mathbf{R}_A-\mathbf{r}|^{-1}|1s(\epsilon)\rangle\} \qquad (46)$$

will be more complete.

By evaluating

$$4\pi\int_0^{r'}1s(\epsilon)r^{-1}1s(\epsilon)r^2dr, \qquad (47)$$

it is found that at $r'=\epsilon$ (in atomic units), the integral $\langle 1s(\epsilon)||\mathbf{R}_A-\mathbf{r}|^{-1}|1s(\epsilon)\rangle$ has $(1-e^{-2})$ of the total value of $2/\epsilon$ a.u. Thus, for a given set of $|\phi_{Aj}\rangle$, the best cancellation occurs when ϵ approximately equals the atomic radius. It was stated previously that the best cancellation in argon–neon occurs for $\epsilon=9$. This is not really quite correct since the value of Δ in Eq. (42) is less in the case $\epsilon=9$ simply because it is the difference of two smaller numbers. In Table XI is displayed the cancellation of the value of $|\mathbf{R}_a-\mathbf{r}|^{-1}$ for the *s* functions of argon. The percentage cancellation is indeed best for $|1s(3)\rangle$, as expected. Also included in Table XI, for comparison purposes, is the 4*s* SCF function. It should be observed that, if we were attempting to fit the higher excited states of the crystal by a $|1s(\epsilon)\rangle$ set, then the set $|\phi_{Aj}\rangle$ might include the 4*s* function.

VII. DISCUSSION

In this paper we have considered two approaches to the calculation of the excitation energy of an impurity in a molecular solid. Consider first the remarkable fact that a simple model Hamiltonian, representing the excited crystal states as hydrogenic, is extremely good for the case of pure Xe despite the size of the orbitals. This result can be rationalized as follows. A simple hydrogenic manifold including the effects of dielectric screening will be accurate, provided that the ratio of the sizes of the lowest hydrogenic excited state and the Wannier function defining the localized wavefunction, is large. Now the solids Ne, Ar, Kr, and Xe are unique in that the conduction bands are very nearly free electron bands because the electron–atom interaction is so small. But when the conduction bands are of the free electron form, the Wannier function is confined to one atomic cell. Thus, even though the lowest hydrogenic orbits in the several solids are only of the order of two lattice spacings, the corresponding Wannier functions are so compact that the cited inequality is achieved. We believe this to be the reason that the spectra of the pure solids Ar, Kr, and Xe may be interpreted as hydrogenic exciton levels. The reader should note that a direct corollary of this argument is that *any impurity states* in a crystal of Xe, Kr, etc., should behave as if the medium served merely as a dielectric continuum. These considerations would be expected to apply best to Xe and worst to Ne. This further implies that the condensed inert gases are very convenient solvents for the identification of Rydberg transitions in molecular spectra.

In the contrary case that the conduction band is not free-electron-like, then the Wannier function spreads over many unit cells and the central-cell correction becomes extremely large. If an impurity introduced into such a system results in a large perturbation, it becomes essential to use the supermolecule formalism. Indeed, even in the most unfavorable case Ar:Ne, we have shown that the supermolecule approximation leads to reasonable agreement with experiment. In other cases, where the corresponding Wannier function may be much larger than the SCF excited-state function, the supermolecule approximation is very much superior and even better results should be obtained. Of course, in intermediate cases it may be necessary to use in the model Hamiltonian a potential more sophisticated than either the SCF atomic potential or the screened Coulomb potential. For these cases the pseudopotential formalism described herein should be useful.

TABLE XI. Expansion of the one-center integral $-\langle 1s(\epsilon) \mid 1/R \mid 1s(\epsilon) \rangle$ in the set of SCF Ar s- symmetry functions, in electron volts.

ϵ	A_j	$\langle 1s(\epsilon) \mid \phi A_j \rangle$ $\times \langle 1s(\epsilon) \mid$ $-1/R \mid \phi A_j \rangle$	Running total	$-\langle 1s(\epsilon) \mid$ $-1/R \mid 1s(\epsilon) \rangle$
3	$1s$	-0.098521	-0.098521	
	$2s$	-0.971253	-1.069774	
	$3s$	-4.002492	-5.072266	
	$4s$	-3.461630	-8.633896	-9.069999
5	$1s$	-0.022170	-0.022170	
	$2s$	-0.245914	-0.268084	
	$3s$	-1.394732	-1.662816	
	$4s$	-3.519817	-5.182633	-5.442000
7	$1s$	-0.008251	-0.008251	
	$2s$	-0.096662	-0.104913	
	$3s$	-0.636000	-0.740913	
	$4s$	···	···	-3.887142
9	$1s$	-0.003932	-0.003920	
	$2s$	-0.047454	-0.051386	
	$3s$	-0.246688	-0.298074	
	$4s$	···	···	-3.023333

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APPENDIX I: MATRIX ELEMENTS FOR THE CHARGE-TRANSFER FORMALISM

In this Appendix we reproduce the definitions of the energy terms used in Tables I–IV. These definitions are discussed more fully in Ref. 6.

For the $\mathcal{H}_{11}$ matrix element, set

$$(\tilde{\chi}_{Aa}(\mathbf{O}) \mid \mathcal{H}(a) \mid \tilde{\chi}_{Aa}(\mathbf{O}))=I_A+I_B+I_C+I_D+I_E, \tag{A1}$$

with

$$I_A=\bar{E}_{Aa}/\eta_A, \tag{A2}$$

$$I_B=-(1/\eta_A)\sum_{Ii}\langle\overline{Aa}\mid Ii\rangle^2 E_{Ii}, \tag{A3}$$

$$I_C=(1/\eta_A)\sum_{I(\neq A)}\langle\overline{Aa}\mid U_{Ia}+C_{Ia}+X_{Ia}\mid\overline{Aa}\rangle, \tag{A4}$$

$$I_D=(1/\eta_A)\sum_{Ii(\neq Aj)}\{\langle\overline{Aa}\mid Ii\rangle^2\langle Ii\mid U_{Aa}+C_{Aa}'+X_{Aa}'\mid Ii\rangle$$
$$-2\langle\overline{Aa}\mid Ii\rangle\langle Ii\mid U_{Aa}+C_{Aa}'+X_{Aa}'\mid\overline{Aa}\rangle\}, \tag{A5}$$

$$I_E=\frac{1}{\eta_A}\sum_{Ii}\sum_{J(\neq A,I)}\{\langle\overline{Aa}\mid Ii\rangle^2\langle Ii\mid U_{Ja}+C_{Ja}+X_{Ja}\mid Ii\rangle$$
$$-2\langle\overline{Aa}\mid Ii\rangle\langle Ii\mid U_{Ja}+C_{Ja}+X_{Ja}\mid\overline{Aa}\rangle\}. \tag{A6}$$

For the $\mathcal{H}_{ij}$ matrix elements, set

$$(\tilde{\chi}_{Aa}(\mathbf{O}) \mid \mathcal{H}(a) \mid \tilde{\chi}_{Nn}(\boldsymbol{\beta}_j))$$
$$=J_A+J_B+J_C+J_D+J_E+J_F+J_G, \tag{A7}$$

with

$$J_A=[1/(\eta_A\eta_N)^{\frac{1}{2}}]\langle\overline{Aa}\mid T_a+U_{Aa}+C_{Aa}'+X_{Aa}'\mid\overline{Nn}\rangle, \tag{A8}$$

$$J_B=[-1/(\eta_A\eta_N)^{\frac{1}{2}}]\sum_{Ii(\neq A,N)}\langle\overline{Aa}\mid Ii\rangle\langle\overline{Nn}\mid Ii\rangle E_{Ii}, \tag{A9}$$

$$J_C=[1/(\eta_A\eta_N)^{\frac{1}{2}}]\langle\overline{Aa}\mid U_{Na}+C_{Na}+X_{Na}\mid\overline{Nn}\rangle, \tag{A10}$$

$$J_D=[1/(\eta_A\eta_N)^{\frac{1}{2}}]\sum_{I(\neq A,N)}\langle\overline{Aa}\mid U_{Ia}+C_{Ia}+X_{Ia}\mid\overline{Nn}\rangle, \tag{A11}$$

$$\begin{aligned}J_E=[1/(\eta_A\eta_N)^{\frac{1}{2}}]\sum_{Ii(\neq Aj)}\{&\langle\overline{Aa}\mid Ii\rangle\langle Nn\mid Ii\rangle\\ &\times\langle Ii\mid U_{Aa}+C_{Aa}'+X_{Aa}'\mid Ii\rangle\\ &-\langle\overline{Nn}\mid Ii\rangle\langle Ii\mid U_{Aa}+C_{Aa}'+X_{Aa}'\mid\overline{Aa}\rangle\\ &-\langle\overline{Aa}\mid Ii\rangle\langle Ii\mid U_{Aa}+C_{Aa}'+X_{Aa}'\mid\overline{Nn}\rangle\},\end{aligned} \tag{A12}$$

$$\begin{aligned}J_F=[-1/(\eta_A\eta_N)^{\frac{1}{2}}]\sum_{Ii(=Aj)}&\langle\overline{Aa}\mid Ii\rangle\\ &\times\langle\overline{Nn}\mid U_{Na}+C_{Na}+X_{Na}\mid Ii\rangle,\end{aligned} \tag{A13}$$

$$\begin{aligned}J_G=[1/(\eta_A\eta_N)^{\frac{1}{2}}]\sum_{Ii(=Aj)}\sum_{J(\neq I,A,N)}\{&\langle\overline{Aa}\mid Ii\rangle\\ &\times\langle\overline{Nn}\mid U_{Ja}+C_{Ja}+X_{Ja}\mid Ii\rangle\\ &+\langle\overline{Nn}\mid Ii\rangle\langle\overline{Aa}\mid U_{Ja}+C_{Ja}+X_{Ja}\mid Ii\rangle\\ &-\langle\overline{Aa}\mid Ii\rangle\langle\overline{Nn}\mid Ii\rangle\langle Ii\mid U_{Ja}+C_{Ja}+X_{Ja}\mid Ii\rangle\}.\end{aligned} \tag{A14}$$

The expansion of the matrix elements $\mathcal{H}_{jj}(j\neq 1)$ is conveniently broken up into two parts

$$\begin{aligned}\sum_{M\geq N}^{N(\beta j)}(\tilde{\chi}_{Nn}(\beta_j)\mid\mathcal{H}(a)\mid\tilde{\chi}_{Mn}(\beta_j))&=(\tilde{\chi}_{Nn}(\beta_j)\mid\mathcal{H}(a)\mid\tilde{\chi}_{Nn}(\beta_j))\\ &+\sum_{M>N}^{N(\beta j)}(\tilde{\chi}_{Mn}(\beta_j)\mid\mathcal{H}(a)\mid\tilde{\chi}_{Nn}(\beta_j)).\end{aligned} \tag{A15}$$

We expand these two parts as follows:

$$(\tilde{\chi}_{Nn}(\beta_j)\mid\mathcal{H}(a)\mid\tilde{\chi}_{Nn}(\beta_j))=K_A+K_B+K_C+K_D+K_E+K_F+K_G, \tag{A16}$$

where

$$K_A=(1/\eta_N)\langle\overline{Nn}\mid T_a+U_{Na}+C_{Na}+X_{Na}\mid\overline{Nn}\rangle, \tag{A17}$$

$$K_B=(-1/\eta_N)\{\sum_{Ii(\neq Aj)}\langle\overline{Nn}\mid Ii\rangle^2E_{Ii}+\sum_{Aj}\langle\overline{Nn}\mid Aj\rangle^2E_{Aj}^*\}, \tag{A18}$$

and

$$\begin{aligned}E_{Aj}^*=E_{Aj}&-\langle Aj(1)Aj(1)\mid r_{12}^{-1}\mid\overline{Aa}(2)\overline{Aa}(2)\rangle\\ &+\langle Aj(1)\overline{Aa}(1)\mid r_{12}^{-1}\mid Aj(2)\overline{Aa}(2)\rangle,\end{aligned} \tag{A19}$$

$$K_C=(1/\eta_N)\langle\overline{Nn}\mid U_{Aa}+C_{Aa}'+X_{Aa}'\mid\overline{Nn}\rangle, \tag{A20}$$

$$K_D=(1/\eta_N)\sum_{I(\neq A,N)}\langle\overline{Nn}\mid U_{Ia}+C_{Ia}+X_{Ia}\mid\overline{Nn}\rangle, \tag{A21}$$

$$\begin{aligned}K_E=(1/\eta_N)\sum_{Ii(\neq Aj)}\{&\langle\overline{Nn}\mid Ii\rangle^2\\ &\times\langle Ii\mid U_{Aa}+C_{Aa}'+X_{Aa}'\mid Ii\rangle,\\ &-2\langle\overline{Nn}|Ii\rangle\langle\overline{Nn}|U_{Aa}+C_{Aa}'+X_{Aa}'|Ii\rangle\},\end{aligned} \tag{A22}$$

$$\begin{aligned}K_F=(-2/\eta_N)\sum_{Ii(=Aj)}&\langle\overline{Nn}\mid U_{Na}+C_{Na}+X_{Na}\mid Ii\rangle\\ &\times\langle\overline{Nn}\mid Ii\rangle,\end{aligned} \tag{A23}$$

$$\begin{aligned}K_G=(1/\eta_N)\sum_{Ii(=Aj)}\sum_{J(\neq A,N,I)}\{&\langle\overline{Nn}\mid Ii\rangle^2\\ &\times\langle Ii\mid U_{Ja}+C_{Ja}+X_{Ja}\mid Ii\rangle\\ &-2\langle\overline{Nn}\mid Ii\rangle\langle\overline{Nn}\mid U_{Ja}+C_{Ja}+X_{Ja}\mid Ii\rangle\}.\end{aligned} \tag{A24}$$

In a similar fashion,

$$\sum_{M>N}^{N(\beta j)}(\chi_{Mn}(\beta_j)\mid\mathcal{H}(a)\mid\chi_{Nn}(\beta_j))=L_A+L_B+L_C+L_D+L_E+L_F+L_G+L_H, \tag{A25}$$

$$L_A=(1/\eta_N)\sum_{M>N}\langle\overline{Nn}\mid T_a+U_{Na}+C_{Na}+X_{Na}\mid\overline{Mn}\rangle, \tag{A26}$$

$$L_B=-(1/\eta_N)\sum_{M>N}\{\sum_{Ii(\neq M,N,A)}\langle\overline{Mn}\mid Ii\rangle\langle\overline{Nn}\mid Ii\rangle E_{Ii}+\sum_{Aj}\langle\overline{Mn}\mid Aj\rangle\langle\overline{Nn}\mid Aj\rangle E_{Aj}^*\}, \tag{A27}$$

$$L_C=(1/\eta_N)\sum_{M>N}\langle\overline{Nn}\mid U_{Mo}+C_{Ma}+X_{Ma}\mid\overline{Mn}\rangle, \tag{A28}$$

$$L_D=(1/\eta_N)\sum_{M>N}\sum_{I(\neq N,M,A)}\langle\overline{Nn}\mid U_{Ia}+C_{Ia}+X_{Ia}\mid\overline{Mn}\rangle, \tag{A29}$$

$$\begin{aligned}L_E=(1/\eta_N)\sum_{M>N}\sum_{Ii}\{&\langle\overline{Mn}\mid Ii\rangle\langle\overline{Nn}\mid Ii\rangle\\ &\times\langle Ii\mid U_{Aa}+C_{Aa}'+X_{Ac}'\mid Ii\rangle\\ &-\langle\overline{Mn}\mid Ii\rangle\langle Ii\mid U_{Aa}+C_{Aa}'+X_{Aa}'\mid\overline{Nn}\rangle\\ &-\langle\overline{Nn}\mid Ii\rangle\langle Ii\mid U_{Aa}+C_{Aa}'+X_{Aa}'\mid\overline{Mn}\rangle\},\end{aligned} \tag{A30}$$

$$\begin{aligned}L_F=-(1/\eta_N)\sum_{M>N}\sum_{Ii}\{&\langle\overline{Nn}\mid Ii\rangle\\ &\times[\langle\overline{Mn}\mid U_{Ma}+C_{Ma}+X_{Ma}\mid Ii\rangle\\ &+\langle\overline{Mn}\mid U_{Na}+C_{Na}+X_{Na}\mid Ii\rangle]\\ &+\langle Mn\mid Ii\rangle[\langle\overline{Nn}\mid U_{Na}+C_{Na}+X_{Na}\mid Ii\rangle\\ &+\langle\overline{Nn}\mid U_{Ma}+C_{Ma}+X_{Ma}\mid Ii\rangle]\\ &-\langle\overline{Mn}|Ii\rangle\langle\overline{Nn}|Ii\rangle[\langle Ii\mid U_{Na}+C_{Na}+X_{Na}\mid Ii\rangle\\ &\qquad+\langle Ii\mid U_{Ma}+C_{Ma}+X_{Ma}\mid Ii\rangle]\},\end{aligned} \tag{A31}$$

$$\begin{aligned}L_G=-(1/\eta_N)\sum_{M>N}\sum_{Ii}\sum_{J(\neq I,M,N)}\{&\langle\overline{Mn}\mid Ii\rangle\\ &\times\langle\overline{Nn}\mid U_{Ja}+C_{Ja}+X_{Ja}\mid Ii\rangle\\ &+\langle\overline{Nn}\mid Ii\rangle\langle\overline{Mn}\mid U_{Ja}+C_{Ja}+X_{Ja}\mid Ii\rangle\\ &-\langle\overline{Mn}|Ii\rangle\langle\overline{Nn}|Ii\rangle\langle Ii|U_{Ja}+C_{Ja}+X_{Ja}|Ii\rangle\},\end{aligned} \tag{A32}$$

$$L_H=(1/\eta_N)\sum_{M>N}\langle\overline{Nn}\mid U_{Aa}+C_{Aa}'+X_{Aa}'\mid\overline{Mn}\rangle. \tag{A33}$$

Note that the latter part of the element $\mathcal{H}_{jj}$ will be identical in form with the element $\mathcal{H}_{ij}$. Therefore, we use the same definitions as above in displaying the terms that make up the matrix element $\mathcal{H}_{ij}$.

It should also be noted that the normalization constant η_N is in general be different for different atomic shells. Therefore, in these equations η_N refers to the geometric mean of the normalization constant for the pair of shells involved, or

$$\eta_N=[\eta(\beta_i)\eta(\beta_j)]^{\frac{1}{2}}. \qquad \text{(A34)}$$

APPENDIX II: WAVEFUNCTIONS USED IN CALCULATIONS

In all the calculations reported herein the SCF wavefunctions were taken as linear combinations of Slater functions.[22] We may write this expansion as

$$\varphi_{j\lambda\alpha}=\sum_p C_{j\lambda p}\chi_{p\lambda\alpha}, \qquad \text{(A35)}$$

where the symmetry species is denoted by λ, the subspecies by α, and p is an index to differentiate between members of the same species. For our purposes we need differentiate only between s functions ($\lambda=0$) and p functions ($\lambda=1$); $\chi_{p\lambda\alpha}$ may be broken up into the radial part and the angular part

$$\chi_{p\lambda\alpha}=R_p(r)\,Y_{\lambda\alpha}(\phi,\theta), \qquad \text{(A36)}$$

where $Y_{\lambda\alpha}(\phi,\theta)$ is a spherical harmonic. $R_p(r)$ is the Slater function

$$R_p(r)=[(2\zeta_p)^{2n_p+1}/(2n_p)!]^{\frac{1}{2}}r^{n_p-1}\exp(-\zeta_p r). \qquad \text{(A37)}$$

Table XII. SCF functions for Ne(^1S) (minimal basis set).[a]

Orbital	n, λ, ζ_p 1, 0, 9.642	 2, 0, 2.879	 2, 1, 2.879	ϵ[b] (a.u.)
1s	0.99735	0.01091	···	−32.66298
2s	−0.25495	1.02937	···	−1.73276
2p	···	···	1.0000	−0.56199

[a] Total energy of the ground-state Ne is −127.8122 a.u. with this basis set.
[b] Orbital energy.

In Table XII are displayed the values of $C_{j\lambda p}$ for the ground-state neon functions.[28] It was found that the tail of the 4s SCF function[11] could be fit rather well by a single Slater function

$$\varphi_{4s}=(4\pi)^{-\frac{1}{2}}[(2\zeta_{4s})^9/8!]^{\frac{1}{2}}r^3\exp(-\zeta_{4s}r),$$
$$\zeta_{4s}=0.845, \qquad \text{(A38)}$$

while the tail of the 3s orbital[11] could be fit by

$$\varphi_{3s}=(4\pi)^{-\frac{1}{2}}[(2\zeta_{3s})^7/6!]^{\frac{1}{2}}r^2\exp(-\zeta_{3s}r),$$
$$\zeta_{3s}=0.822. \qquad \text{(A39)}$$

Using the program described in Ref. 25, the SCF functions for the ^1P state of argon were calculated using a minimal basis set. It is this SCF result referred to in Table IX. This analytical SCF wavefunction was used for the calculations reported herein because it was quite similar to the numerical SCF function of Ref. 11 and because numerical integrations are thereby avoided. The Slater function of (A38) was found to give comparable results for those integrals where only the behavior of the tail is important. The $C_{j\lambda p}$ values for these functions are given in Table XIII.

The 3s fit (A39) was orthogonalized to the ground-state Ne functions (Table XI). The core functions of a Ne(^1P) atom change very little from the wavefunctions of Ne(^1S) atom, so that this orthogonalized 3s function was very similar to the true SCF 3s function.

Table XIII. SCF functions for Ar (^1P) (minimal basis set).[a]

Orbital	n, λ, ζ_p 1, 0, 17.5075	 2, 0, 6.1152	 3, 0, 2.6218	 4, 0, 0.7885	 2, 1, 7.0041	 3, 1, 2.3672	ϵ[b]
1s	0.99759	0.00798	−0.00169	0.00020	···	···	−118.85968
2s	0.32480	1.05497	0.01646	−0.00194	···	···	−12.40508
3s	0.10743	−0.39826	1.07383	0.00926	···	···	−1.44825
4s	0.01485	−0.05555	0.16116	−1.00982	···	···	−0.13158
2p	···	···	···	···	0.98607	0.05474	−9.68545
3p	···	···	···	···	0.28773	−1.02573	−0.80673

[a] Total atom energy is −525.42986 a.u. with this basis set.
[b] Orbital energy in atomic units.

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[28] P. S. Bagas, T. L. Gilbert, C. C. J. Roothaan, and H. Cohen (to be published).