future by improvement of the potential field and also by taking into account the intermolecular interactions in the crystalline state.

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APPENDIX

The internal coordinates and the intermediate symmetry coordinates corresponding to Eqs. (1) and (7) of Ref. 13, respectively, are given in Tables VII and VIII. The numbering of the atoms is shown in Fig. 6. Here the number of the chemical unit, j, is omitted for simplicity in the notations, $C_I(j)$, $C_I(j+1)$, $C_I(j-1)$, $\cdots$. Thus $C_I(+1)$ and $C_I(-1)$ represent $C_I(j+1)$ and $C_I(j-1)$, respectively.

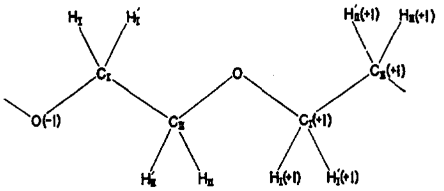

FIG. 6. Atom numbering adopted for the polyethylene oxide molecule.

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Ion-Pair Exciton States and the Optical Spectrum of Crystalline Neon

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The energy of the first electronic transition in crystalline neon has been calculated in the Heitler–London scheme. The calculation differs from previous work in that the effects of ionized exciton states are formulated as charge transfer states in which the excited electron resides on neighboring neons while the $(1s)^2(2s)^2(2p^5)$ hole remains on the central neon. Only the $\Gamma(k=0)$ point in k space is considered, and spin–orbit coupling is neglected.

When correction is made for the nonstationary character of an exciton in solids, the predicted blue shift of 0.25 eV seems to be in reasonable agreement with the trend of spectral shifts of other rare-gas solids.

I. INTRODUCTION

IT is commonly supposed that the electronic states of molecules entering into the formation of a molecular solid or liquid are little affected by the surrounding medium. For the description of a very few gross phenomena this approximation is adequate; for the study of energy transfer, spectral shifts, photoionization, exciton dynamics, and a host of other subjects, it is obviously inadequate.

The earliest studies of the optical spectra of crystalline solids were made by Frenkel[1] and Peierls.[2] These studies were concerned primarily with tightly bound states which are characterized by zero-order wavefunctions which do not overlap seriously with the surrounding medium. In this case the spectrum of the molecule in the crystal differs only slightly from that of the isolated molecule. Extension of the theory by Davydov[3] to the case of crystals with more than one molecule per unit cell; and subsequent experimental and theoretical work by Craig,[4] McClure,[5] and others has shown that the lowest excited states of crystals of aromatic molecules are often aptly described as Frenkel exciton states. Even for these most favorable cases, it is often necessary to include the effects of configuration interaction and crystal field induced mixing of configurations, since the absorption intensities and polarization ratios often deviate markedly from the simplest oriented gas model.

In 1937, Wannier[6] considered those crystal excitations which could be described as arising from the manifold of states of a bound hole–electron pair. In a sense, these states are analogous to the Rydberg states of molecules and may be characterized by zero-order wavefunctions which extensively overlap with the surrounding medium. Wannier excitons have a hydrogenlike spectrum and the role of the surrounding medium is to dielectrically screen the Coulomb interaction. Experimental studies of Cu_2O[7] and of impurity

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* NSF cooperative fellow.

[1] J. I. Frenkel, Phys. Rev. **37,** 17 (1931).

[2] R. Peierls, Ann. Physik **13,** 905 (1932).

[3] A. S. Davydov, *Theory of Molecular Excitations* (translated by M. Kasha and M. Oppenheimer) (McGraw-Hill Book Company, Inc., New York, 1962).

[4] See D. Craig and P. Hobbins, J. Chem. Soc. **1955,** 539.

[5] See, for example, D. McClure, Solid State Phys, **8,** 1 (1959); **9,** 399 (1959).

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

[7] S. Nikitine, G. Perny, and M. Sieskind, Compt. Rend. **238,** 1987 (1954).

donor centers in semiconductors indicate that Wannier excitons are an apt description of diffuse but bound states in a high-dielectric-constant medium.

Frenkel excitons[1] and Wannier excitons[6] clearly represent two extremes of behavior. In this paper we consider an intermediate case in which the overlap of the wavefunction of the excited molecule and the medium is very large, but where the wavefunction still does not penetrate far enough into the medium to validate a dielectric screening approximation. Thus, it will be necessary to examine in some detail the nature of the lowest excited states of the constituent molecules and of their interaction with the surrounding crystal. In particular, we focus attention on the role of configuration mixing of the neutral exciton with the lowest charge transfer (or ion-pair exciton) state. This latter state is characterized by a charge distribution with a hole on one molecule and an electron on a nearest-neighbor molecule, and is obviously only one of the many possible states intermediate between the tightly bound Frenkel exciton and the weakly bound Wannier exciton. As will be shown in other work, ion-pair exciton states can play an important role in energy transfer, exciton dynamics and the spectroscopy of molecular solids.

In the analysis presented in this paper we do not compute the band structure of the solid. Instead, we use a "supermolecule" approximation in which some central atom and a large number of neighbors (~12 to 135) are taken to comprise a representation of the full crystal. The wavefunction for this subsystem is constructed in the molecular orbital utilizing the symmetry inherent in the structure. In the approach sketched, all calculations are made in the direct space of the lattice. The reader should note that the procedure we use is related to the Wigner–Seitz approximation[8] in the theory of metals.

We reserve for the final section a detailed description of the results of the analysis.

II. FORMULATION OF THE CALCULATION

Consider a sample of crystalline neon. The normal crystal structure for neon (and other rare-gas solids) is fcc,[9] with each neon atom surrounded by 12 other neon atoms at 5.8124 a_0, six at 8.2200 a_0, 24 at 10.0674 a_0, and so on. It is these first three shells surrounding an excited neon atom that play the most important role in this calculation. To describe this system we start with antisymmetrized product (AP) wavefunctions made up of orthogonal one-electron functions. Because the overlap between ground-state wavefunctions on different centers is very small (~0.01), it is assumed that the SCF ground-state wavefunctions are accurate representations of the crystal ground-state wavefunction.[10] Thus, for the ground state of the crystal in the zeroth order, we take the representation[11]

$$^1\phi_g = \mathcal{A}\varphi_{Aa}'\varphi_{Aa}\prod_{I(=A)}\prod_{i(\neq a)}\varphi_{Ii}'\varphi_{Ii}, \tag{1}$$

where $\mathcal{A}$ represents the antisymmetrization operator, φ_{Aa} is the ground-state wavefunction belonging to Atom A (the central neon) and the ath atomic function, φ_{Aa}' refers to the $\chi_{Aa}\alpha$ function and φ_{Aa} to the $\chi_{Aa}\beta$ function, where χ_{Aa} is the spatial part of the wavefunction. Of course, it is the ground-state wavefunction from which excitation is to take place; in the case of Ne this is a $2p$ function. The product in Eq. (1) is over all the atoms in the crystal, where I refers to the nuclear site and i refers to the wavefunction centered on that site. Equation (1) represents a singlet ground-state. In the excited state the zeroth-order wavefunction may be represented by the four wavefunctions which define the singlet and triplet states (we assume the crystal Hamiltonian to be spin free throughout this treatment).

$$^1\phi_e = \mathcal{A}(1/\sqrt{2})\{\psi_{Aa}'\varphi_{Aa} - \psi_{Aa}\varphi_{Aa}'\}\prod_{I(=A)}\prod_{i(\neq a)}\varphi_{iI}'\varphi_{Ii}, \tag{2a}$$

$$^3\phi_e = \mathcal{A}\begin{bmatrix} \psi_{Aa}'\varphi_{Aa}' \\ (1/\sqrt{2})\{\psi_{Aa}'\varphi_{Aa} + \psi_{Aa}\varphi_{Aa}'\} \\ \psi_{Aa}\varphi_{Aa} \end{bmatrix} \times \prod_{I(=A)}\prod_{i(\neq a)}\varphi_{Ii}'\varphi_{Ii}. \tag{2b}$$

The ψ_{Aa} refers to the excited-state wavefunction which in dilute gas phase would be the SCF $3s$ neon wavefunction. We leave ψ_{Aa} general as there is expected to be a modification of the wavefunction in the solid state. When spin–orbit coupling is neglected the only energy difference between the singlet and triplet states arises from the electrostatic exchange splitting $2K$ where[12]

$$K = (\psi_{Aa}(1)\varphi_{Aa}(1) \mid r_{12}^{-1} \mid \psi_{Aa}(2)\varphi_{Aa}(2)). \tag{3}$$

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[8] E. Wigner and F. Seitz, Phys. Rev. **43**, 804 (1933); **46**, 509 (1934).

[9] E. R. Dobbs and G. O. Jones, Rept. Progr. Phys. **20**, 516 (1957). The reader should note that by lattice constant we mean the distance half-way along the side of a unit cell. It has been pointed out by A. Gold and R. S. Knox that the change of the van der Waals forces will be of the same order of magnitude as our calculated blue shift. [See for example, A. Gold, J. Chem. Phys. Solids **18**, 218 (1961).]

[10] A. Gold, Phys. Rev. **124**, 1740 (1961). After making a rather elaborate calculation on a similar system, it was concluded that any changes of these ground-state wavefunctions were so small that they could be neglected.

[11] The notation to be used for the summations is as follows: A sum such as Σ_{Ii} is to be taken to mean a double sum over the i functions centered on the I different nuclear sites. On occasion it is convenient to include the ground-state functions of central neon atoms in such a sum. In that case the notation $\Sigma_{Ii(=Aj)}$ is used. This should be taken to mean summation over only the occupied ground-state functions of the central neon atom (i.e., $1s$, $2s$, $2p$). When these are to be expressly excluded, the notation $\Sigma_{Ii(\neq Aj)}$ is used.

[12] The notation $(||)$ means integration over the spin and space parts of a function throughout this paper except where noted otherwise. The notation $\langle Ii|$ is used for SCF functions so that integration over the space and spin parts of these functions would be written $\langle Ii|f|Jj\rangle$ or $\langle IiIi|g|JjJj\rangle$ where f and g are one- and two-electron operators as usual.

For the neon atom the $^1P-{}^3P$ energy difference in the pure LS coupling scheme is only 0.18 eV. Keeping this in mind we carry out our calculation for the function

$$\Psi_e=\mathcal{A}\psi_{Aa}\varphi_{Aa}'\prod_{I(=A)}\prod_{i(\neq a)}\varphi_{Ii}'\varphi_{Ii}, \tag{4}$$

realizing that the electrostatic splitting must eventually be accounted for. The purpose of this calculation is not to study the splitting between the singlet and triplet substates of the excited state, but rather to study the change of the center of gravity of the absorption lines on transition from free atom to solid. The SCF $3s$ neon function differs somewhat in the singlet and triplet states,[13] but since orthogonalization and expansion in a basis set alter the excited-state function anyway, we arbitrarily neglect this small difference and choose to work with the singlet $3s$ function. Certainly this choice leads to only slight differences in the values of matrix elements and to no difference in the general approach.

Roothaan[14] showed in 1951 that if a SCF calculation is based on AP wavefunctions and one of the molecular orbitals[15] (MO) is written as a linear combination of other functions (which may or may not be atomic orbitals), the vibrational principle leads to the matrix equation

$$\mathbf{Fx}=\mathbf{Sx}\epsilon \tag{5}$$

where

$$F_{ij}=(\chi_i\,|\,F\,|\,\chi_j).$$

As usual, F is the Hartree–Fock operator equal to the sum of kinetic energy and nuclear attraction operators, plus the Coulombic and exchange potentials due to the charge distribution of the other electrons present. F is a one-electron operator although the terms in it are sometimes due to the interactions of two electrons. The χ's are members of the basis set that construct the F matrix. In order that this variational treatment be valid for excited states, it is necessary that the eigenfunctions of the F matrix be orthogonal to the ground-state functions. If this precaution is not observed, the wavefunction calculated converges to the ground-state wavefunction. It is necessary, therefore, to choose the set χ to be orthogonal to the ground-state functions. Also, the set χ should be chosen such that the elements F_{ij} and F_{ii} are nonvanishing and of the same order of magnitude, respectively. In a first-order approximate calculation, this condition precludes the use of χ's similar to ground-state functions as the basis set for expansion of the excited-state functions. As a quantitative guide, the F_{ij} element would be expected to be small if the charge distribution $\chi_i\,\chi_j$ is small over all space. Thus, the magnitude of the overlap integral $(\chi_i\,|\,\chi_j)$ may be used as a rough criterion of the necessity for the addition of more functions to the basis set.

It is clear that we have now but to define our basis set and calculate the F matrix for this crystal problem. There are, in a sense two alternatives which may be used. A set of functions centered on the excited atom with different values of the principle quantum number and the orbital exponent may be used or, alternatively, a set of functions with the same or similar radial extent can be centered on neighboring atoms. It is this latter course which is pursued herein. These charge-transfer states or ion-pair excitons are quite similar to the Wannier exciton in physical content, but are different in that functions centered on different lattice sites are not orthogonal. The charge-transfer states cited are not constructed from Bloch functions in this calculation, but the resulting energy matrix is easily shown to be expressible in terms of the energy matrix based on Wannier functions (see Appendix I).

We wish to diagonalize the energy matrix in the excitation wave representation $E(\mathbf{K},\boldsymbol{\beta})$ (following the notation of Wannier).[16] Here $\mathbf{K}$ refers to the wave vector of the electron–hole pair and in this calculation is taken to be zero as it is this part of the band which is most important in an optical absorption experiment. The vector $\boldsymbol{\beta}$ refers to the electron–hole separation and defines the position of the center of the charge-transfer function. Of course, the matrix is not diagonal in the representation based on the position of the excited atom; taking this into account adds a term of the form of a dipole–dipole interaction which falls off as R^{-3}, where R is the separation of the two excited atoms.[17] This interaction energy is calculated in the continuum approximation.[18]

The calculation described herein proceeded as follows: First, a basis set of the form

$$\psi_{Aa}=U(\mathbf{O})\tilde{\chi}_{Aa}+U(|\,\boldsymbol{\beta}_1\,|)\sum_{N=1}^{12}\tilde{\chi}_{Nn}, \tag{6}$$

was used, where $U(\boldsymbol{\beta})$ is the coefficient of the function located a vector distance $\boldsymbol{\beta}$ from the hole and is determined by the diagonalization of the F matrix discussed

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[13] A. Gold and R. Knox, Phys. Rev. **113,** 834 (1959).

[14] C. C. J. Roothaan, Rev. Mod. Phys. **23,** 69 (1951). It should be noted that the Hartree–Fock equations are not this simple for the open-shell $(1s)^2(2s)^2(2p)^53s$ configuration. The error in using a closed-shell formalism is quite small (a 0.05–0.10 eV) compared to terms neglected in the crystal Hamiltonian as defined [see, for example, C. C. J. Roothaan, Rev. Mod. Phys. **32,** 179 (1960)].

[15] In our context, molecular orbital means any function extending over more than one nuclear site. The treatment that follows is similar to that for a Ne–Ne$_{12}$ "molecule" or, more correctly, an Ne–Ne$_N$ ($N\sim$42–135) molecule as this many centers were involved in the orthogonalization. This approach is characterized as the "supermolecule" formalism.

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

[17] R. Knox, Solid State Phys. Suppl. **5,** 1 (1963).

[18] W. R. Heller and A. Marcus, Phys. Rev. **84,** 809 (1951). Neglecting exchange between states differing in the position of the excited atom is probably a poor approximation for these diffuse wavefunctions. A. Gold and R. S. Knox have suggested that exchange may be as important as the dipole terms. Since our interest is not in the band structure of solid neon we believe our neglect to be justified within the 1–1½ eV error estimate of this calculation (see Appendix II.D, for example).

above.[19] $\boldsymbol{\beta}_1$ is the vector distance to the first shell. The functions $\tilde{\chi}_{Aa}$ and $\tilde{\chi}_{Nn}$ are orthogonal to all occupied valence and core orbitals and are described below. In this calculation the lattice parameter (defined here as the distance half-way along the unit cell) was varied so that the approximate behavior of these states could be studied as the nuclei were moved further apart. The results of this study are somewhat inconclusive, as the F matrix is not even approximately diagonal in this limited representation. For this calculation 12 nearest neighbors are used as sites for the charge-transfer state and a crystal containing 43 atoms is used for the SCF potential.

The second calculation was made for the equilibrium lattice separation with the basis set

$$\psi_{Aa}=U(\mathbf{O})\tilde{\chi}_{Aa}+U(|\boldsymbol{\beta}_1|)\sum_{N=1}^{12}\tilde{\chi}_{Nn}+U(|\boldsymbol{\beta}_2|)\sum_{M=1}^{6}\tilde{\chi}_{Mn}$$
$$+\ (|\boldsymbol{\beta}_3|)\sum_{P=1}^{24}\tilde{\chi}_{Pn}. \qquad (7)$$

The effect of the further extension of the basis set on the lowest excited states can be tested directly as can the structure of the higher excited states. Specifically, it is possible to see if a hydrogenic energy level series results from the direct diagonalization of the F matrix. Hydrogenic level structure has been observed recently in solid xenon.[20]

The Schmidt orthogonalized functions $\tilde{\chi}_{Aa}$ and $\tilde{\chi}_{Nn}$ are defined as follows[11]:

$$\tilde{\chi}_{Aa}=(1/\eta_A^{\frac{1}{2}})\{\bar{\varphi}_{Aa}-\sum_{Ii}\langle\overline{Aa}\mid Ii\rangle\varphi_{Ii}\},$$
$$\eta_A=\{1-\sum_{Ii}\langle\overline{Aa}\mid Ii\rangle^2\}, \qquad (8a)$$

$$\tilde{\chi}_{Nn}=(1/\eta_N^{\frac{1}{2}})$$
$$\times\{\bar{\varphi}_{Nn}-\sum_{Ii(\neq Aj)}\langle\overline{Nn}\mid Ii\rangle\varphi_{Ii}-\sum_{Aj}\langle\overline{Nn}\mid Aj\rangle\varphi_{Aj}\},$$
$$\eta_N=\{1-\sum_{Ii(\neq Aj)}\langle\overline{Nn}\mid Ii\rangle^2-\sum_{Aj}\langle\overline{Nn}\mid Aj\rangle^2\}, \qquad (8b)$$

where $\bar{\varphi}_{Aa}$ and $\bar{\varphi}_{Nn}$ refer to the $3s$ SCF neon functions.[21]

It is now necessary to define the HF crystal Hamiltonian. We use a notation that stresses the physical nature of the Hamiltonian, i.e., the presence of a number of neutral atoms. Consider the definitions

$$T_a\equiv-(\hbar^2/2m)\nabla_a^2, \qquad (9a)$$
$$U_{Ia}\equiv(-Z_I\,|\,e\,|^2/|\,\mathbf{R}_I-\mathbf{r}_a\,|), \qquad (9b)$$
$$C_{Ia}\equiv|\,e\,|^2\sum_{i=1}^{Z_I}\int\frac{|\,\varphi_{Ii}(i)\,|^2}{|\,r_i-r_a\,|}d\tau_i, \qquad (9c)$$

$$X_{Ia}(Kk,Jj)\equiv-|\,e\,|^2\sum_{i=1}^{Z_I}\int\frac{\varphi_{Ii}(a)\varphi_{Kk}{}^*(a)\varphi_{Ii}(i)\varphi_{Jj}(i)\,d\tau_i}{\varphi_{Kk}{}^*(a)\varphi_{Jj}(a)\;|\,\mathbf{r}_i-\mathbf{r}_a\,|}. \qquad (9d)$$

The atomic functions we use are all eigenfunctions of the HF atomic equation, so that

$$[T_i+U_{Ii}+C_{Ii}+X_{Ii}(Ii,Ii)]\varphi_{Ii}=E_{Ii}\varphi_{Ii}. \qquad (10)$$

The one-electron crystal Hamiltonian can now be written[22]

$$\mathcal{H}(a)=T_a+U_{Aa}+C_{Aa}+X_{Aa}(\ )$$
$$+\sum_{I(\neq A)}[U_{Ia}+C_{Ia}+X_{Ia}(\ )]. \qquad (11)$$

The matrices which are to be diagonalized have the following types of elements:

$$H_{11}\equiv(\tilde{\chi}_{Aa}\mid\mathcal{H}(a)\mid\tilde{\chi}_{Aa}), \qquad (12)$$
$$H_{1j}\equiv H_{j1}\equiv N(\boldsymbol{\beta}_j)[\tilde{\chi}_{Aa}(\mathbf{O})\mid\mathcal{H}(a)\mid\tilde{\chi}_{Nn}(\boldsymbol{\beta}_j)], \qquad (13)$$

where $N(\boldsymbol{\beta}_j)$ is the number of atoms at separation $\boldsymbol{\beta}_j$ from the Ath site. To designate $\tilde{\chi}_{Nn}$ functions centered on the various shells we use $\chi_{Nn}(\boldsymbol{\beta}_j)$ which should not be taken to mean that χ_{Nn} is an explicit function of $\boldsymbol{\beta}_j$: ,

$$H_{jj}=N(\boldsymbol{\beta}_j)\sum_{M\geq N}^{N(\beta j)}\ [\tilde{\chi}_{Nn}(\boldsymbol{\beta}_j)\mid\mathcal{H}(a)\mid\tilde{\chi}_{Mn}(\boldsymbol{\beta}_j)] \qquad (14)$$

$$H_{ij}=H_{ji}\equiv N(\boldsymbol{\beta}_i)\sum_{M>N}^{N(\beta j)}[\tilde{\chi}_{Nn}(\boldsymbol{\beta}_i)\mid\mathcal{H}(a)\mid\tilde{\chi}_{Mn}(\boldsymbol{\beta}_j)]. \qquad (15)$$

The overlaps S_{11}, S_{1j}, S_{jj}, S_{ij} are defined as above except that $\mathcal{H}(a)$ is replaced by unity. The matrix equation is just that of Eq. (5) except that the symbol H is used here instead of F. Expansion of the above matrix elements leads to several terms that require further discussion.

(1) Terms such as $\langle Ii\mid\mathcal{H}(a)\mid Jj\rangle$, where $\langle Ii\mid$ and $\langle Jj\mid$ are ground-state functions, are ignored because the charge distribution $\varphi_{Ii}(a)\ \varphi_{Jj}(a)$ is small everywhere.

(2) Terms such as

$$\langle Ii\mid Ta+U_{Ia}+C_{Ia}+X_{Ia}(Ii,Ii)\mid Ii\rangle$$

are equal to E_{Ii}. If one extracts from the C_{Ia} and $X_{Ia}(Ii,\ Ii)$ sum that pair of terms due to the Iith

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[19] Because of the crystal structure of neon there are 12 functions χ_{Nn} which are equidistant from the Ath site. The spherical symmetry of $\tilde{\chi}_{Aa}$ implies that all twelve of $\tilde{\chi}_{Nn}$ mix equally. The same is true of the basis set described by Eq. (7).

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

[21] It should be emphasized that these $3s$ SCF functions are for an excited, neutral neon atom. When an electron is put in such a $3s$ orbital on a neutral neon to form a "Ne⁻" ion it suffers a large repulsive force which is offset by the attraction of the neighboring $(1s)^2(2s)^2(2p)^5$ hole. [See Ka and Kc, Eq. (30a) and (30c), respectively, and their values in Table VII.] It is not at all obvious that the true Ne^- orbitals would be a superior basis set.

[22] The arguments of χ_{Aa} and χ_{Ia} are not written as these potentials are not defined unless the functions on which they are to operate are first defined.

function we find that

$$\int\frac{|\varphi_{Ii}(i)|^2}{|\mathbf{r}_i-\mathbf{r}_a|}d\tau_i-\int\frac{\varphi_{Ii}{}^*(a)\varphi_{Ii}(a)\varphi_{Ii}(i)\varphi_{Ii}(i)}{\varphi_{Ii}{}^*(a)\varphi_{Ii}(a)\,|\mathbf{r}_i-\mathbf{r}_a|}d\tau_i=0, \quad (16)$$

and the potential left is the same as the HF potential.[23]

(3) Terms such as

$$\langle Ii\,|\,Ta+U_{Ja}+C_{Ja}+X_{Ja}(Ii,Jj)\,|\,Jj\rangle$$

are approximated by $\langle Ii\,|\,Jj\rangle E_{Jj}$ even though the exchange potential is changed. In actual calculations this approximation is made only if $\langle Ii\,|$ is one of the spatially diffuse excited state functions. By expansion of the function $\langle Ii\,|$ in the set of states $\langle J_k\,|$ one can show that the approximation is valid if

$$\sum_{k\neq j}^{\infty}\langle Ii\,|\,Jk\rangle[\langle Jk\,|\,X_{Ia}(Jk,Jj)\,|\,Jj\rangle \\ -\langle Jk\,|\,X_{Ia}(Jj,Jj)\,|\,Jj\rangle] \quad (17)$$

is vanishingly small.

(4) The physical situation we deal with involves a delocalized electron interacting with all the surrounding neutral atoms, plus the positive hole at the Ath site, and the formal potential must reflect this description. Indeed, such a representation is derived from the potential as defined for the general element

$$\langle Kk\,|\,U_{Aa}+C_{Aa}+X_{Aa}(Kk,Ii)\,|\,Ii\rangle$$

by extracting from the sum in C_{Aa} and $X_{Aa}(Kk,Ii)$ those terms due to the $\langle\overline{Aa}\,|$ function, which are

$$\int\frac{|\bar{\varphi}_{Aa}(a)|^2}{|\mathbf{r}_a-\mathbf{r}_a|}d\tau_a-\int\frac{\bar{\varphi}_{Aa}(a)\varphi_{Kk}{}^*(a)\varphi_{Aa}{}^*(a)\varphi_{Ii}(a)d\tau_a}{\varphi_{Kk}{}^*(a)\varphi_{Ii}(a)\,|\mathbf{r}_a-\mathbf{r}_a|}=0. \quad (18)$$

We use the symbols C_{Aa}' and $X_{Aa}'(\cdots)$ to signify that the ath electron has been removed so that at large separations the total Aath potential has the limit $-|e|^2/|\mathbf{R}_A-\mathbf{r}_a|$.

(5) There will be terms such as the following:

$$\langle Kk\,|\,Ta+U_{Ka}+C_{Ka}+X_{Ka}(Kk,Ii) \\ +U_{Ia}+C_{Ia}+X_{Ia}(Kk,Ii)\,|\,Ii\rangle.$$

Using the approximation mentioned in (3) this could be evaluated as either

$$\langle Kk\,|\,Ii\rangle E_{Kk}+\langle Kk\,|\,U_{Ia}+C_{Ia}+X_{Ia}(Kk,Ii)\,|\,Ii\rangle$$

or

$$\langle Kk\,|\,Ii\rangle E_{Ii}+\langle Kk\,|\,U_{Ka}+C_{Ka}+X_{Ka}(Kk,Ii)\,|\,Ii\rangle.$$

(When the full crystal Hamiltonian is used, there are more terms than displayed above, but the idea remains the same.) The energy operator must be Hermitian, of course, so we take one-half the sum of the two expressions above as an Hermitian average. This procedure was used only in the lattice variation calculation. It was found that the approximation

$$\langle Kk\,|\,Ta+C_{Ia}+X_{Ia}+U_{Ia}\,|\,Ii\rangle\approx\langle Kk\,|\,Ii\rangle E_{Ii} \quad (19)$$

was somewhat better when $\langle Kk\,|$ was one of the $3s$ functions and $\langle Ii\,|$ a ground-state function. This is easily understood in that the charge density of $\varphi_{Ii}\bar{\varphi}_{Nn}$ is more like $|\varphi_{Ii}|^2$ in the region of the Ith site than it is like $|\bar{\varphi}_{Nn}|^2$ in the region of the Nth site. The approximation above was also found to be quite good if both $\langle Ii\,|$ and $\langle Kk\,|$ were excited state functions. (see Appendix II.) With the use of Conditions (1)–(5) the various matrix elements can be expanded as follows:

$$[\tilde{\chi}_{Aa}(\mathbf{O})\,|\,\mathcal{H}(a)\,|\,\tilde{\chi}_{Aa}(\mathbf{O})]=I_A+I_B+I_C+I_D+I_E, \quad (20)$$

$$I_A=\bar{E}_{Aa}/\eta_A, \quad (21a)$$

$$I_B=-(1/\eta_A)\sum_{Ii}\langle\overline{Aa}\,|\,Ii\rangle^2E_{Ii}, \quad (21b)$$

$$I_C=(1/\eta_A)\sum_{I(\neq A)}\langle\overline{Aa}\,|\,U_{Ia}+C_{Ia}+X_{Ia}\,|\,\overline{Aa}\rangle, \quad (21c)$$

$$I_D=(1/\eta_A)\sum_{Ii(\neq Aj)}\{\langle\overline{Aa}\,|\,Ii\rangle^2\langle Ii\,|\,U_{Aa}+C_{Aa}'+X_{Aa}'\,|\,Ii\rangle \\ -2\langle\overline{Aa}\,|\,Ii\rangle\langle Ii\,|\,U_{Aa}+C_{Aa}'+X_{Aa}'\,|\,\overline{Aa}\rangle\}, \quad (21d)$$

$$I_E=(1/\eta_A)\sum_{Ii}\sum_{J(\neq A,I)}\{\langle\overline{Aa}\,|\,Ii\rangle^2\langle Ii\,|\,U_{Ja}+C_{Ja}+X_{Ja}\,|\,Ii\rangle \\ -2\langle\overline{Aa}\,|\,Ii\rangle\langle Ii\,|\,U_{Ja}+C_{Ja}+X_{Ja}\,|\,\overline{Aa}\rangle\}. \quad (21e)$$

As mentioned in the preceding paragraph there are two difinitions for the element H_{ij}.

If, instead of a Hermitian average we define a non-Hermitian average as follows:

$$[\tilde{\chi}_{Aa}(\mathbf{O})\,|\,\mathcal{H}(a)\,|\,\tilde{\chi}_{Nn}(\boldsymbol{\beta}_j)] \\ =J_A+J_B+J_C+J_D+J_E+J_F+J_G. \quad (22)$$

Then

$$J_A=[1/(\eta_A\eta_N)^{\frac{1}{2}}]\langle\overline{Aa}\,|\,Ta+U_{Aa}+C_{Aa}'+X_{Aa}'\,|\,\overline{Nn}\rangle, \quad (23a)$$

$$J_B=[-1/(\eta_A\eta_N)^{\frac{1}{2}}]\sum_{Ii(\neq A,N)}\langle\overline{Aa}\,|\,Ii\rangle\langle\overline{Nn}\,|\,Ii\rangle E_{Ii}, \quad (23b)$$

$$J_C=[1/(\eta_A\eta_N)^{\frac{1}{2}}]\langle\overline{Aa}\,|\,U_{Na}+C_{Na}+X_{Na}\,|\,\overline{Nn}\rangle, \quad (23c)$$

$$J_D=[1/(\eta_A\eta_N)^{\frac{1}{2}}]\sum_{I(\neq A,N)}\langle\overline{Aa}\,|\,U_{Ia}+C_{Ia}+X_{Ia}\,|\,\overline{Nn}\rangle, \quad (23d)$$

$$J_E=[1/(\eta_A\eta_N)^{\frac{1}{2}}]\sum_{Ii(\neq Aj)}\{\langle\overline{Aa}\,|\,Ii\rangle\langle\overline{Nn}\,|\,Ii\rangle \\ \times\langle Ii\,|\,U_{Aa}+C_{Aa}'+X_{Aa}'\,|\,Ii\rangle \\ -\langle\overline{Nn}\,|\,Ii\rangle\langle Ii\,|\,U_{Aa}+C_{Aa}'+X_{Aa}'\,|\,\overline{Aa}\rangle \\ -\langle\overline{Aa}\,|\,Ii\rangle\langle Ii\,|\,U_{Aa}+C_{Aa}'+X_{Aa}'\,|\,\overline{Nn}\rangle\}, \quad (23e)$$

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[23] This is no longer true if the ϕ_{Ii} function is unoccupied in the ground state, i.e. $\langle\overline{Nn}\,|$.

$$J_F=[-1/(\eta_A\eta_N)^{\frac{1}{2}}]\sum_{Ii(=Aj)}\langle\overline{Aa}\,|\,Ii\rangle$$
$$\times\langle\overline{Nn}\,|\,U_{Na}+C_{Na}+X_{Na}\,|\,Ii\rangle, \tag{23f}$$

$$J_G=[1/(\eta_A\eta_N)^{\frac{1}{2}}]\sum_{Ii(=Aj)}\sum_{J(\neq I,A,N)}\{\langle\overline{Aa}\,|\,Ii\rangle$$
$$\times\langle\overline{Nn}\,|\,U_{Ja}+C_{Ja}+X_{Ja}\,|\,Ii\rangle$$
$$+\langle\overline{Nn}\,|\,Ii\rangle\langle\overline{Aa}\,|\,U_{Ja}+C_{Ja}+X_{Ja}\,|\,Ii\rangle$$
$$-\langle\overline{Aa}\,|\,Ii\rangle\langle\overline{Nn}\,|\,Ii\rangle\langle Ii\,|\,U_{Ja}+C_{Ja}+X_{Ja}\,|\,Ii\rangle\}. \tag{23g}$$

In the case that the Hermitian average is taken, the H_{1j} element is

$$[\tilde{\chi}_{Aa}(\mathbf{O})\,|\,\mathcal{H}(a)\,|\,\tilde{\chi}_{Nn}(\boldsymbol{\beta}_j)]$$
$$=J_A'+J_B'+J_C'+J_D'+J_E'. \tag{24}$$

It was found that, to a good approximation,

$$\langle\overline{Aa}\,|\,Ta+U_{Na}+C_{Na}+X_{Na}(\overline{Aa},\overline{Nn})\,|\,\overline{Nn}\rangle$$
$$=\langle\overline{An}\,|\,\overline{Nn}\rangle\bar{E}_{Nn}^{*}, \tag{25}$$

where

$$\bar{E}_{Nn}^{*}=\bar{E}_{Nn}+|e|^2\langle\overline{Nn}(a)\overline{Nn}(a)\,|\,r_{ia}^{-1}\,|\,Nn(i)Nn(i)\rangle$$
$$-|e|^2\langle\overline{Nn}(a)Nn(a)\,|\,r_{ia}^{-1}\,|\,\overline{Nn}(i)Nn(i)\rangle \tag{26}$$

and

$$\langle Nn\,|=\varphi_{2p},$$

$$J_A'=[1/(\eta_A\eta_N)^{\frac{1}{2}}]\{\langle\overline{Aa}\,|\,\overline{Nn}\rangle-\sum_{Ii}\langle\overline{Aa}\,|\,Ii\rangle\langle\overline{Nn}\,|\,Ii\rangle\}$$
$$\times\{\tfrac{1}{2}(\bar{E}_{Aa}+\bar{E}_{Nn}^{*}\}, \tag{27a}$$

$$J_B'=[-1/2(\eta_A\eta_N)^{\frac{1}{2}}]\sum_{Ii(=Aj)}[\![\langle\overline{Nn}\,|\,Ii\rangle$$
$$\times\langle Ii\,|\,U_{Ia}+C_{Ia}+X_{Ia}\,|\,\overline{Aa}\rangle$$
$$+\langle\overline{Aa}\,|\,U_{Aa}+C_{Aa}'+X_{Aa}'\,|\,Ii\rangle$$
$$+\langle\overline{Aa}\,|\,Ii\rangle\langle\overline{Nn}\,|\,U_{Na}+C_{Na}+X_{Na}\,|\,Ii\rangle$$
$$+2\langle\overline{Nn}\,|\,U_{Aa}+C_{Aa}'+X_{Aa}'\,|\,Ii\rangle$$
$$+\langle Ii\,|\,U_{Ia}+C_{Ia}+X_{Ia}\,|\,\overline{Nn}\rangle$$
$$-2\langle\overline{Aa}\,|\,Ii\rangle\langle\overline{Nn}\,|\,Ii\rangle\langle Ii\,|\,U_{Aa}+C_{Aa}'+X_{Aa}'\,|\,Ii\rangle]\!], \tag{27b}$$

$$J_C'=[1/2(\eta_A\eta_N)^{\frac{1}{2}}]\{\langle\overline{Nn}\,|\,U_{Na}+C_{Na}+X_{Na}\,|\,\overline{Aa}\rangle$$
$$+\langle\overline{Aa}\,|\,U_{Aa}+C_{Aa}'+X_{Aa}'\,|\,\overline{Nn}\rangle\}, \tag{27c}$$

$$J_D'=[1/(\eta_A\eta_N)^{\frac{1}{2}}]\sum_{Jj(\neq A,N)}\langle\overline{Nn}\,|\,U_{Ja}+C_{Ja}+X_{Ja}\,|\,\overline{Aa}\rangle, \tag{27d}$$

$$J_E'=[-1/(\eta_A\eta_N)^{\frac{1}{2}}]\sum_{Ii(\neq Aj)}\sum_{J(\neq I,A,N)}\{\langle\overline{Nn}\,|\,Ii\rangle$$
$$\times\langle\overline{Aa}\,|\,U_{Ja}+C_{Ja}+X_{Ja}\,|\,Ii\rangle$$
$$+\langle\overline{Aa}\,|\,Ii\rangle\langle\overline{Nn}\,|\,U_{Ja}+C_{Ja}+X_{Ja}\,|\,Ii\rangle$$
$$-\langle\overline{Aa}\,|\,Ii\rangle\langle\overline{Nn}\,|\,Ii\rangle\langle Ii\,|\,U_{Ja}+C_{Ja}+X_{Ja}\,|\,Ii\rangle\}. \tag{27e}$$

The expansion of the matrix elements $H_{jj}(j\neq1)$ is conveniently broken up into two parts:

$$\sum_{M\geq N}^{N(\beta j)}[\tilde{\chi}_{Nn}(\boldsymbol{\beta}_j)\,|\,\mathcal{H}(a)\,|\,\tilde{\chi}_{Mn}(\boldsymbol{\beta}_j)]$$
$$=[\tilde{\chi}_{Nn}(\boldsymbol{\beta}_j)\,|\,\mathcal{H}(a)\,|\,\tilde{\chi}_{Nn}(\boldsymbol{\beta}_j)]$$
$$+\sum_{M>N}^{N(\beta j)}[\tilde{\chi}_{Mn}(\boldsymbol{\beta}_j)\,|\,\mathcal{H}(a)\,|\,\tilde{\chi}_{Nn}(\boldsymbol{\beta}_j)]. \tag{28}$$

We expand these two parts as follows:

$$[\tilde{\chi}_{Nn}(\boldsymbol{\beta}_j)\,|\,\mathcal{H}(a)\,|\,\tilde{\chi}_{Nn}(\boldsymbol{\beta}_j)]$$
$$=K_A+K_B+K_C+K_D+K_E+K_F+K_G, \tag{29}$$

where

$$K_A=(1/\eta_N)\langle\overline{Nn}\,|\,Ta+U_{Na}+C_{Na}+X_{Na}\,|\,\overline{Nn}\rangle, \tag{30a}$$

$$K_B=-(1/\eta_N)\{\sum_{Ii(\neq Aj)}\langle\overline{Nn}\,|\,Ii\rangle^2E_{Ii}$$
$$+\sum_{Aj}\langle\overline{Nn}\,|\,Aj\rangle^2E_{Aj}^{*}\}, \tag{30b}$$

and

$$E_{Aj}^{*}=E_{Aj}-\langle Aj(1)Aj(1)\,|\,r_{12}^{-1}\,|\,\overline{Aa}(2)\overline{Aa}(2)\rangle$$
$$+\langle Aj(1)\overline{Aa}(1)\,|\,r_{12}^{-1}\,|\,Aj(2)\overline{Aa}(2)\rangle, \tag{30b$'$}$$

$$K_C=(1/\eta_N)\langle\overline{Nn}\,|\,U_{Na}+C_{Aa}'+X_{Aa}'\,|\,\overline{Nn}\rangle, \tag{30c}$$

$$K_D=(1/\eta_N)\sum_{I(\neq A,N)}\langle\overline{Nn}\,|\,U_{Ia}+C_{Ia}+X_{Ia}\,|\,\overline{Nn}\rangle, \tag{30d}$$

$$K_E=(1/\eta_N)\sum_{Ii(\neq Aj)}\{\langle\overline{Nn}\,|\,Ii\rangle^2$$
$$\times\langle Ii\,|\,U_{Aa}+C_{Aa}'+X_{Aa}'\,|\,Ii\rangle$$
$$-2\langle\overline{Nn}\,|\,Ii\rangle\langle\overline{Nn}\,|\,U_{Aa}+C_{Aa}'+X_{Aa}'\,|\,Ii\rangle\}, \tag{30e}$$

$$K_F=(-2/\eta_N)\sum_{Ii(=Aj)}\langle\overline{Nn}\,|\,U_{Na}+C_{Na}+X_{Na}\,|\,Ii\rangle$$
$$\times\langle\overline{Nn}\,|\,Ii\rangle, \tag{30f}$$

$$K_G=(1/\eta_N)\sum_{Ii(=Aj)}\sum_{J(\neq A,N,I)}\{\langle\overline{Nn}\,|\,Ii\rangle^2$$
$$\times\langle Ii\,|\,U_{Ja}+C_{Ja}+X_{Ja}\,|\,Ii\rangle$$
$$-2\langle\overline{Nn}\,|\,Ii\rangle\langle\overline{Nn}\,|\,U_{Ja}+C_{Ja}+X_{Ja}\,|\,Ii\rangle\}. \tag{30g}$$

In a similar fashion,

$$\sum_{M>N}^{N(\beta j)}[\tilde{\chi}_{Mn}(\boldsymbol{\beta}_j)\,|\,\mathcal{H}(a)\,|\,\tilde{\chi}_{Nn}(\boldsymbol{\beta}_j)]$$
$$=L_A+L_B+L_C+L_D+L_E+L_F+L_G+L_H, \tag{31}$$

$$L_A=(1/\eta_N)\sum_{M>N}\langle\overline{Nn}\,|\,Ta+U_{Na}+C_{Na}+X_{Na}\,|\,\overline{Mn}\rangle, \tag{32a}$$

$$L_B=-(1/\eta_N)\sum_{M>N}\{\sum_{Ii(\neq M,N,A)}\langle\overline{Mn}\,|\,Ii\rangle\langle\overline{Nn}\,|\,Ii\rangle E_{Ii}$$
$$+\sum_{Aj}\langle\overline{Mn}\,|\,Aj\rangle\langle\overline{Nn}\,|\,Aj\rangle E_{Aj}^{*}\}, \tag{32b}$$

$$L_C=(1/\eta_N)\sum_{M>N}\langle\overline{Nn}\,|\,U_{Ma}+C_{Ma}+X_{Ma}\,|\,\overline{Mn}\rangle \tag{32c}$$

$$L_D=(1/\eta_N)\sum_{M>N}\sum_{I(\neq N,M,A)}\langle\overline{Nn}\,|\,U_{Ia}+C_{Ia}+X_{Ia}\,|\,\overline{Mn}\rangle, \tag{32d}$$

$$\begin{aligned}L_E=(1/\eta_N)\sum_{M>N}\sum_{Ii}&\langle\overline{Mn}\,|\,Ii\rangle\langle\,|\overline{Nn}\,Ii\rangle\\&\times\langle Ii\,|\,U_{Aa}+C_{Aa}'+X_{Aa}'\,|\,Ii\rangle\\&-\langle\overline{Mn}\,|\,Ii\rangle\langle Ii\,|\,U_{Aa}+C_{Aa}'+X_{Aa}'\,|\,\overline{Nn}\rangle\\&-\langle\overline{Nn}\,|\,Ii\rangle\langle Ii\,|\,U_{Aa}+C_{Aa}'+X_{Aa}'\,|\,\overline{Mn}\rangle,\end{aligned} \tag{32e}$$

$$\begin{aligned}L_F=-(1/\eta_N)\sum_{M>N}\sum_{Ii}\{&\langle\overline{Mn}\,|\,Ii\rangle\\&\times\langle\overline{Nn}\,|\,U_{Na}+C_{Na}+X_{Na}\,|\,Ii\rangle\\&-\langle\overline{Nn}\,|\,Ii\rangle\langle\overline{Mn}\,|\,U_{Ma}+C_{Ma}+X_{Ma}\,|\,Ii\rangle\},\end{aligned} \tag{32f}$$

$$\begin{aligned}L_G=-(1/\eta_N)\sum_{M>N}\sum_{Ii}\sum_{J}\{&2\langle\overline{Mn}\,|\,Ii\rangle\\&\times\langle\overline{Nn}\,|\,U_{Ja}+C_{Ja}+X_{Ja}\,|\,Ii\rangle\\&-\langle\overline{Mn}\,|\,Ii\rangle\langle\overline{Nn}\,|\,Ii\rangle\langle Ii\,|\,U_{Ja}+C_{Ja}+X_{Ja}\,|\,Ii\rangle\},\end{aligned} \tag{32g}$$

$$L_H=(1/\eta_N)\sum_{M>N}\langle\overline{Nn}\,|\,U_{Aa}+C_{Aa}'+X_{Aa}'\,|\,\overline{Mn}\rangle \tag{32h}$$

Note that the latter part of the element H_{jj} will be identical in form with the element H_{ij}. Therefore we use the same definitions as above in displaying the terms that make up the matrix element H_{ij} in the next section.

III. NUMERICAL CALCULATIONS

As can be seen by inspection of the various quantities that make up the matrix elements, it is necessary to evaluate a multicentered wavefunction over a multicentered potential. Most of the important terms are two-center integrations which can be performed analytically and quickly with the use of high-speed computers once the appropriate programs are developed. Many of the sums are quite lengthy and complex, but techniques were developed to handle them quickly and for rather general cases. The 1, 1 element gives the orbital energy of the neon 3*s* wavefunction without charge transfer. There appear in this element no important three-center integrals that need be evaluated, so the computational error involved in determining the zeroth-order energy is very small.

Unfortunately, three-center terms are of significance in the other matrix elements. Throughout this work the Mulliken approximation was used for these integrals, i.e., it was assumed that

$$\bar{\varphi}_{Aa}\bar{\varphi}_{Nn}\approx\tfrac{1}{2}\langle\overline{Aa}\,|\,\overline{Nn}\rangle\{\bar{\varphi}_{Aa}\bar{\varphi}_{Aa}+\bar{\varphi}_{Nn}\bar{\varphi}_{Nn}\} \tag{33}$$

for the purposes of evaluating three-center integrals. When this approximation was checked against an actual numerical three-center integration of certain potential terms, the agreement obtained was remarkably good. We estimate that the maximum uncertainty in the three-center terms is of the order of ±10%, but a valid test of this uncertainty must await the development of general three-center integral computation programs.

As a matter of convenience the tails of the excited-state wavefunctions were fitted to Slater functions. This fitting introduces no error in principle, as the inner nodes of the 3*s* function have no effect on the interatomic energies. The best fit was found to be

$$\varphi_{3s}=[2\zeta_{3s}/4\pi(6!)]^{\frac{1}{2}}r^2\exp(-\zeta_{3s}r), \tag{34}$$

where $\zeta_{3s}=0.822$. It was found that the nodes in the 3*s* function do have a strong effect on certain integrals, such as $\langle Nn\,|\,U_{Ma}+C_{Ma}+X_{Ma}\,|\,Mn\rangle$. These nodes were added by orthogonalizing the Slater fit of the 3*s* function to the ground-state *s* functions described below. (See Appendix II.)

The reader will note that many of the terms to be evaluated are Coulombic in nature and have opposite signs. Rather than evaluate large nuclear and electron Coulomb integrals and then take the difference, a total Coulomb potential was derived. This potential fell off approximately exponentially with increasing distance. To carry through the calculation one must have some analytic form for the ground state wavefunctions. For convenience, the analytic form is taken to be a combination of Slater functions, so that formulas derived by Roothaan[24] can be used directly. The neon ground-state functions were taken from an SCF calculation using a minimal basis set and were supplied by Bagas *et al.*[25] These functions are

$$\begin{aligned}\varphi_{1s}&=C_{1,1s}\chi_{1s}+C_{2,1s}\chi_{2s},\\\varphi_{2s}&=C_{1,2s}\chi_{1s}+C_{2,2s}\chi_{2s},\\\varphi_{2p}&=\chi_{2p},\\\chi_{1s}&=[(2\zeta_1)^3/2!]^{\frac{1}{2}}\exp(-\zeta_1 r)\,Y_0^0(\theta,\vartheta),\\\chi_{2s}&=[(2\zeta_2)^5/4!]^{\frac{1}{2}}r\exp(-\zeta_2 r)\,Y_0^0(\theta,\vartheta),\\\chi_{2p_m}&=[2\zeta_2/4!]^{\frac{1}{2}}r\exp(-\zeta_2 r)\,Y_1^m(\theta,\vartheta),\\\zeta_1&=9.642,\qquad\zeta_2=2.879,\\C_{1,1s}&=0.99735,\qquad C_{2,1s}=0.01091,\\C_{1,2s}&=-0.25495,\qquad C_{2,2s}=1.02937.\end{aligned}$$

The total Coulombic potential of an atom was assumed to be spherically symmetric. In the case of the potential $U_{Aa}+C_{Aa}'$, the total potential was derived from an average of the three degenerate configurations

$$(1s)^2(2s)^2(2p_{+1})^2(2p_{-1})^2(2p_0)^1,$$

$$(1s)^2(2s)^2(2p_{+1})^2(2p_{-1})^1(2p_0)^2$$

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[24] C. C. J. Roothaan, J. Chem. Phys. **19**, 1445 (1951). See especially Eqs. (12) and (33).

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

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

L.C.[a]	I_A	I_B	I_C	I_D	I_E	H_{11}
(1)	−5.597	11.323	−7.696	0.999	0	−0.971
(2)	−5.152	6.180	−4.325	0.551	0	−2.746
(3)	−4.910	3.413	−2.453	0.280	0	−3.670

[a] Here and in Tables II–V, L. C. refers to the lattice constant as follows: (1) = 3.71 a_0, (2) = 4.11 a_0, (3) = 4.51 a_0.

TABLE II. Terms in H_{12} (in electron volts).

L.C.	J_A'	J_B'	J_C'	$J_D'^+$	J_E'	$H_{12/12}$
(1)	−0.641	5.877	−1.858	−3.857	0	−0.479
(2)	−0.551	2.979	−1.527	−2.030	0	−1.129
(3)	−0.486	1.461	−1.285	−0.991	0	−1.301

and

$$(1s)^2(2p_{+1})^1(2p_{-1})^2(2p_0)^2.$$

This potential is also spherically symmetric.

The exchange potential cannot be put into analytic form, as it depends not only on the atom involved but also on the particular functions being integrated. All two-center exchange calculations were performed with a numerical integration program. Again, all three-center exchange terms were computed using the Mulliken approximation.

Certain properties of the charge distributions may be exploited to advantage in the calculation. For example, the charge distribution $\bar{\varphi}_{Aa}\varphi_{Ii}$ is centered around the Ith nuclear site. Thus, the following approximations are quite good:

$$\langle \overline{Aa} \mid U_{Aa}+C_{Aa}'+X_{Aa}'(\overline{Aa}, Ii) \mid Ii \rangle \approx -\mid e \mid^2 \langle \overline{Aa} \mid Ii \rangle / \mid \mathbf{R}_A - \mathbf{R}_I \mid, \tag{36}$$

$$\langle Nn \mid U_{Na}+C_{Na}+X_{Na}(\overline{Nn}, Ii) \mid Ii \rangle \approx 0. \tag{37}$$

Direct calculation of the latter term displayed leads to values of the order of 10^{-6} eV or less.

A. Variation of Lattice Constant

It is of interest to study the effect of changes of the crystal lattice constant on the calculated excited-state energy level. The experimentally determined lattice constant[9] is 4.11 a_0, so we chose this value along with 3.71 and 4.51 a_0. The calculation for the lattice constant 3.71 a_0 is somewhat suspect as the approximations discussed above are probably much poorer for this case than for the larger lattice spacings. Nevertheless, this study shows that the charge transfer mechanism partially compensates for rather gross changes of the environment and tends to keep the excited state orbital energy constant, thereby making understandable the fact that such a gross difference of environments as exists between the gaseous and solid states results in only minor shifts of the absorption spectrum.

The values of the terms H_{11}, H_{12}, H_{22}, S_{12}, S_{22}, are given in Tables I through IV for the various lattice parameters. In Table V are displayed the results of diagonalizing the 2×2 matrix along with the change of energy due to the inclusion of the first charge-transfer state. It is seen that the energy lowering due to this charge-transfer state does not diminish as the lattice constant is increased. It is this fact that led to the further expansion of the charge-transfer basis set.

B. Increased Charge-Transfer Basis Set

For this computation the basis set described by Eq. (7) is used. Because the basis set is expanded the size of the crystal used in the computation had to be increased. Whereas the calculation described in Sec. A uses a 43-atom lattice (1+12+6+24=43), this calculation uses a 135-atom lattice (1+12+6+24+12+24+8+48=135). These functions are centered on atoms in the first three shells about some chosen atom (located at 5.8124, 8.2200, 10.0674 a_0). It can be noted that the quantities previously calculated in Sec. A agree quite well with the new calculations. The disagreement is due to the different crystal size and somewhat poorer approximations used for the former computation. The matrix elements are displayed in Tables VI through X.

In Table XI the advantages derived by increasing the size of the basis set are clearly demonstrated. Except for the 2×2 case the matrix equation was

TABLE III. Terms in H_{22} (in electron volts).

L.C.	K_A	K_B	K_C	K_D	K_E	K_F	K_G	Sum	$H_{22}/12$
(1)	3.106	11.384	−6.656	−7.094	0.702	0	0	1.442	12.657
(2)	2.860	6.236	−5.448	−3.977	0.355	0	0	0.026	5.393
(3)	2.725	3.466	−4.653	−2.250	0.183	0	0	−0.529	7.194
L. C.	L_A	L_B	L_C	L_D^+	L_E	L_F	L_G	L_H^+	Sum
(1)	10.537	48.059	2.212	−24.537	2.549	0	0	−27.605	11.215
(2)	8.548	24.418	1.575	−11.982	1.4000	0	0	−18.592	5.367
(3)	6.473	17.013	1.128	−5.498	0.763	0	0	−12.156	7.723

TABLE IV. Values of overlap.

L.C.	$S_{12}/12$[a]	$S_{22}/12$[b]
(1)	0.62613	5.377
(2)	0.53867	4.495
(3)	0.47455	3.623

[a] $S_{12}=[1/(\eta_A\eta_N)^{\frac{1}{2}}]\{\langle\overline{Nn}|\overline{Aa}\rangle-\Sigma_{Ii}\langle\overline{Aa}|Ii\rangle\langle\overline{Nn}|Ii\rangle\}$.

[b] $S_{22}=1.0000+\{\Sigma_{M>N}[\langle\overline{Mn}|\overline{Nn}\rangle-\Sigma_{Ii}\langle\overline{Mn}|Ii\rangle\langle\overline{Nn}|Ii\rangle]\}$.

TABLE V. Eigenvalues, energy change due to charge-transfer states.

L.C.	$3s_{\text{crystal}}$	$\Delta\epsilon_{CT}$[a]	BS[b]
(1)	0.980	0.009	3.62
(2)	−2.856	0.110	1.74
(3)	−3.823	0.153	0.78

[a] $\Delta\epsilon_{CT}=|H_{11}-\epsilon_{\text{crystal}}|$, all energies in electron volts.

[b] BS=blue shift. The zeroth-order prediction of the change of the first absorption line of crystalline neon.

solved by multiplying on the left by S^{-1} and diagonalizing. That is,

$$\mathbf{Hx}=\mathbf{Sx}\epsilon \tag{38}$$

becomes

$$\mathbf{S}^{-1}\mathbf{Hx}=\mathbf{Ix}\epsilon, \tag{39}$$

which leads to the secular equation

$$\det\{\mathbf{S}^{-1}\mathbf{H}-\mathbf{I}\epsilon\}=0. \tag{40}$$

There would appear to be nothing hydrogenic about either the $U(\mathfrak{Z}_j)$ or the higher excited states. However, such a conclusion is only weakly justified as the higher roots of a variational treatment provide at best a very poor approximation to the true excited states of the system. This observation is further discussed in the following section.

IV. CONCLUSIONS

The calculations of Sec. IIIA serve to illustrate the physical effects of the crystal environment on Rydberg-like excited states but give a very poor indication of the predicted absorption energy. The reason for this is made clear in Sec. IIIB where the introduction of a larger basis set makes a spectacular change in the predicted upper limit of the 3*s* (crystal) energy level. However, the results of Sec. IIIA indicate that one need not be concerned that small changes in the crystal lattice will result in huge differences in the absorption energy of rare gas solids. This is especially useful to know for the case of impurity-state calculations where nuclear configurations must be estimated. Such changes in the lattice parameter as used in that calculation would require very high pressures and are probably much larger than the "lattice changes" resulting from vibrational motions. One may make a very crude estimate of the experimentally observed linewidths from the slope of the *E*-vs-lattice-parameter plot. If the experimentally observed absorption line samples nuclear configurations which are ±2% of the equilibrium nuclear configuration, then a linewidth of the order of 0.4 eV would be observed. Such a calculation, performed for the full basis set, could give a rather accurate estimate of linewidth arising from nuclear motion.

The results of Sec. IIIB are at first very puzzling. One would expect, *a priori*, that those functions with the largest off-diagonal elements would result in the greatest decrease of orbital energy. Exactly the opposite effect is observed. Also there is a regular variation in the sign of the coefficients in the eigenvectors. We feel this behavior can be understood in the following way: The principle interaction of the 3*s*-like state is with the atoms of the first shell (see Appendix II). Thus the variation of the energy of the excited state depends on the variation of the wavefunction in the immediate vicinity of the first shell nuclei. Such a variation is efficiently achieved by surrounding each of these first-shell atoms with functions centered on its nearest neighbors. In the case of the 2×2 matrix there are four neighbors of each first-shell atom plus the central atom involved in the basis set. In the 3×3 matrix there are seven neighbors and for the 4×4 case there are eleven neighbors in the total basis set. Thus if the atoms in the fourth shell (at 11.62 a_0 from the central atom, 12 atoms) were added to the basis set we would expect the resulting orbital energy to be the lowest minimum reached by this procedure. In Table XII is demonstrated the fact that all 11 functions are required in order to reach the energy minimum reported here. One sees that using a 2×2 matrix with a different basis set than the charge transfer functions centered on the first shell also results in small energy lowering.

Such a result suggests that the effect of the environment on the electron–hole interaction through some

TABLE VI. H_{1j} elements (in electron volts).

J_A	J_B	J_C	J_D	J_E	J_F	J_G	N	Matrix element	
−2.7305	3.0028	0.3144	−2.1392	0.2465	0	0	2	−1.3060	$H_{12}/12$
−2.3575	2.4644	0.0876	−1.2465	0.2115	0	0	14	−0.8405	$H_{13}/6$
−0.8940	1.6132	0.0297	−0.68856	0.1287	0	0	20	−0.1890	$H_{14}/24$

TABLE VII. H_{jj} elements, $j\neq 1$ (in electron volts).

K_A	K_B	K_C	K_D	K_E	K_F	K_G	N	Sum$_1$	$H_{jj}=\text{sum}_1+\text{sum}_2$	
2.8602	6.1929	−5.4498	−4.0045	0.3843	0	0	2	−0.0169	$5.4606=H_{22}/12$	
2.8602	6.1929	−3.7378	−4.2946	0.3693	0	0	14	+1.390	$4.1861=H_{33}/16$	
2.8602	6.1929	−3.0281	−4.3237	0.3198	0	0	20	+2.0211	$13.635\ =H_{44}/24$	
L_A	L_B	L_C	L_D^+	L_E	L_F	L_G	L_H	N	Range of M	sum$_2$
9.8293	24.4026	1.5755	−13.0010	1.4000	0	0	−18.7289	2	3–13	5.4775
0.9881	4.1726	0.0960	−1.4837	0.3144	0	0	−1.2913	14	15–19	2.7961
6.1856	18.6670	0.8868	−8.9616	1.1133	0	0	−6.5487	20	21–43	11.3424

macroscopic dielectric constant has probably been overemphasized. It is probably more nearly true that for these intermediate exciton cases the dielectric effect is small. This should be tested by allowing the excited state charge distribution to mix with the highly excited neutral states of the surrounding neon atoms. It would be inconsistent to include such effects in this calculation for several reasons: (1) the computational uncertainty is greater than the expected magnitude of the effect, (2) as pointed out in Appendix II the neon ground-state functions are not the best possible functions, and to calculate polarization of the neon atoms using these functions could result in large error. Thus one would have to use better SCF functions for the neon orbitals.

These calculations also indicate that one would have to use charge-transfer states quite far removed from the excited atom before a Wannier solution would be valid. One of the conditions for the validity of the hydrogen solution to the matrix diagonalization problem is that all off-diagonal elements vanish, or alternatively that β be a good quantum number. This would appear not to be true of the H_{1j} elements until $|\beta|\approx$ 14–16 a_0.

Since the supermolecule approach described herein allows $|\beta|\approx 10\ a_0$, no meaningful statements can be made concerning the energy-level structure of the higher virtual states. It would be of interest to compare the solutions found here with those found by solving Wannier's difference equation.[16] It seems quite likely that a strongly oscillating solution would be found so long as one did not approximate the difference equation by a differential equation. This comparison is now under study.

Figure 1 illustrates the large modification effected on a $3s$ (gas) neon function when it is orthogonalized to become a zero-order $3s$ (crystal) function. Figure 1 shows only the effect of orthogonalizing a $3s$ function to the s functions of a nearest neighbor. Also shown on the ψ_{Aa}-function plot (at a few points) is the ψ_{Aa}-function for the complete charge-transfer function. It is seen that for this particular plot only very slight changes appear in the ψ_{Aa}-function after the addition of the charge-transfer states.

The calculations reported in this paper lead to the following conclusions:

(1) The computation of the first excited state of crystalline Ne in the Heitler–London scheme without charge transfer and using the Schmidt orthogonalization procedure leads to a predicted blue shift of ∼1.9 eV.

(2) Inclusion of a 42-atom charge-transfer basis set leads to a predicted blue shift of about 0.5 eV.

(3) Inclusion of the exciton shift for Ne leads to a relatively small (0.26 eV) decrease of the predicted blue shift (see Appendix III). The contribution of the exciton shift becomes progressively more important in going from Ne to Xe. Thus a final calculated blue shift would be of the order of 0.25 eV.

(4) We have demonstrated the importance of configuration-interaction effects on the energy of the excited state of solid Ne. The contribution of ion pair exciton states within the supermolecule approximation leads to a sizeable decrease in the predicted blue shift of the first absorption.

Many interesting features of the Rydberg states deserve further study. These include the relative importance of charge transfer, configuration interaction (including, of course, continuum contributions), the effect of the singlet and triplet exciton migration, long range polarization of the medium, the change of van der Waals forces,[9] and so on. One would like to be able to go smoothly from the description of crystal excited states as Frenkel excitons (no delocalization in the excited-state wavefunction) to charge-transfer or ion-

TABLE VIII. H_{11} element (in electron volts).

I_A	I_B	I_C	I_D	I_E	H_{11}
−5.1536	6.1929	−4.3527	0.5508	0	−2.7626

TABLE IX. H_{ij} element (in electron volts).

L_A[a]	L_B	L_C	L_D[b]	L_E	L_F	L_G	L_H[b]	N	Range of M	$H_{ij}/N(\beta_i)$
4.1238	10.3900	0.6887	−5.6107	0.6813	0	0	−6.6233	2	14–19	$3.6498 = H_{23}/12$
10.8911	31.2577	1.6475	−15.0951	2.0350	0	0	−16.1411	2	20–43	$14.5951 = H_{24}/12$
9.7434	26.7222	1.4958	−13.9352	1.6745	0	0	−11.5242	14	20–43	$14.1765 = H_{34}/6$

[a] $\sum_{M/N} \langle \overline{Nn} \mid \overline{Mn} \rangle \bar{E}_{Nn}^{*}/\eta_N$, where $\bar{E}_{Nn}^{*}/\eta_N = 2.8602$.

[b] Three-center term approximated by the Mulliken approximation.

TABLE X. S_{ij} terms.

$(1/\eta_N) \sum_{m>n} \langle \overline{Nn} \mid \overline{Mn} \rangle$	$(1/\eta_N) \langle \overline{Nn} \mid \overline{Nn} \rangle \delta_{ij}$	$-(1/\eta_N) \sum_{m>n} \sum_{Ii} \langle \overline{Mn} \mid Ii \rangle \langle \overline{Nn} \mid Ii \rangle$	N	Range of M	$S^{a}/N(\beta_i)$
					$1.0 = S_{11}$
0.5342		−0.0570	1	2–13	$0.4772 = S_{12}/12$
0.2895		−0.0478	1	14–19	$0.2417 = S_{13}/6$
0.1591		−0.0302	1	20–43	$0.1289 = S_{14}/24$
3.8502	1.1203	−0.4638	2	3–13	$4.5067 = S_{22}/12$
1.6153		−0.1971	2	14–19	$1.4182 = S_{23}/12$
4.2661		−0.5969	2	20–43	$3.6692 = S_{24}/12$
0.3871	1.1203	−0.0806	14	15–19	$1.4268 = S_{33}/6$
3.8165		−0.5050	14	20–43	$3.3115 = S_{34}/6$
2.4229	1.1203	−0.3581	20	21–43	$3.1851 = S_{44}/24$

[a] Each of these elements must be multiplied by a factor $N(\beta_i)$ (where β_i refers to the shell that contains the Nth atom) before being entered in the S matrix. The same procedure should be followed for the elements of the H matrix in the previous tables.

TABLE XI. Effect of expanding basis set.

BSS[a]	$U(\mathbf{0})$[b]	$U(\lvert\beta_1\rvert)$[b]	$U(\lvert\beta_2\rvert)$[b]	$U(\lvert\beta_3\rvert)$[b]	ϵ_1	ϵ_2	ϵ_3	ϵ_4	$\Delta\epsilon_{CT}$[c]	ΔE[d]
2	0.9999	−0.00696			−2.7626	7.2538			0.0	1.84
3	0.9924	−0.0512	0.1119		−2.906	0.118	7.447		0.1434	1.69
4	0.9636	−0.0408	0.2547	−0.0694	−4.095	0.0451	4.124	8.749	1.3324	0.51

[a] BSS = Basis set size. The basis set size is increased starting from the first shell and going to the third shell.

[b] $U(\beta_j)$ is the coefficient described by Eq. (7) for the lowest root of the secular equation, ϵ_1. $\lvert\beta_1\rvert = 5.8124\ a$; $\lvert\beta_2\rvert = 8.2200\ a$; $\lvert\beta_3\rvert = 10.0674\ a$.

[c] $\Delta\epsilon_{CT} = \lvert H_{11} - \epsilon_1 \rvert$, all energies in electron volts.

[d] $\Delta E = \epsilon_1 - \bar{E}_{Aa}$ and corresponds to the first-order prediction of the shift of the adsorption line in the solid.

pair excitons (moderate delocalization) to Wannier excitons (extreme delocalization with binding) to continuum states (complete delocalization).

We believe the principal result of this work to be the demonstration of the importance of ion-pair excitons in the spectroscopy of molecular solids. Undoubtedly, there are many other systems and many more phenomena in which important contributions by these states cannot be neglected. One such case, to be discussed in a separate paper, is the Davydov splittings of some excited electronic states of aromatic crystals.

TABLE XII. The effect on orbital energy of surrounding first-shell atoms with charge-transfer functions.

Size of basis set	No. of neighbors of a first-shell atom	Shells involved in basis set	ϵ_1(eV)
2	4	1	−2.763
2	2	2	−2.776
2	4	3	−3.098
3	6	1, 3	−2.906
4	10	1, 2, 3	−4.095

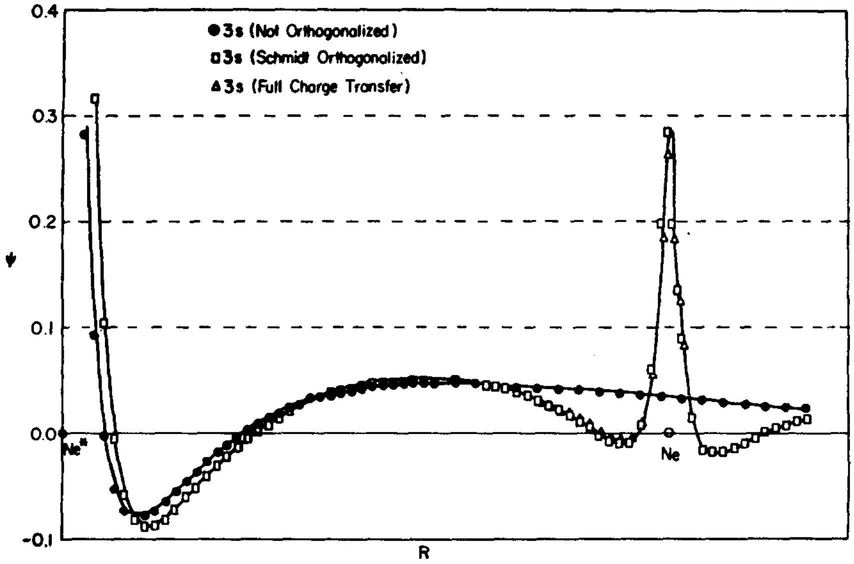

FIG. 1. Orthogonalization effects on the neon 3*s* orbital.

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APPENDIX I. RELATION OF LOCALIZED CHARGE-TRANSFER STATES TO WANNIER FUNCTION

Consider the formation of a Bloch state for the first excited state of a crystal. We choose to use the atomic excited state ϕ to construct the Bloch function and have already orthogonalized ϕ to all the ground state localized functions (by the Schmidt procedure for example). As Löwdin has pointed out, the Bloch sum over atomic functions is not correct unless the atomic functions are orthogonal. If the real a.f.'s are not orthogonal, one may use the orthogonalized functions given by[26]

$$\boldsymbol{\varphi}=(\mathbf{1}+\mathbf{S})^{-\frac{1}{2}}\boldsymbol{\phi} \qquad \text{(AI.1)}$$

or

$$\varphi_\gamma=\sum_\mu (1+S)_{\gamma\mu}{}^{-\frac{1}{2}}\phi_\mu. \qquad \text{(AI.2)}$$

The index μ refers to the position in the lattice as the ϕ's are all identical. The proper Bloch function is, therefore,

$$\chi k=N^{-\frac{1}{2}}\sum_\mu \exp(i\mathbf{k}\cdot\boldsymbol{\mu})\varphi_\mu. \qquad \text{(AI.3)}$$

The localized or Wannier function formed from such a Bloch sum is

$$a_\nu=N^{-\frac{1}{2}}\sum_k^N \exp(-i\mathbf{k}\cdot\boldsymbol{\nu})\chi k$$

$$=N^{-1}\sum_k^N\sum_\mu^N \exp[i\mathbf{k}\cdot(\boldsymbol{\mu}-\boldsymbol{\nu})]\varphi_\mu, \qquad \text{(AI.4)}$$

but

$$\sum_k^N \exp[i\mathbf{k}\cdot(\mu-\nu)]=N\delta_{\mu\nu}, \qquad \text{(AI.5)}$$

$$a_\nu=\varphi_\nu=\sum_\mu (1+S)_{\nu\mu}{}^{-\frac{1}{2}}\phi_\mu, \qquad \text{(AI.6)}$$

or

$$\mathbf{a}=(\mathbf{1}+\mathbf{S})^{-\frac{1}{2}}\boldsymbol{\phi}. \qquad \text{(AI.7)}$$

It is interesting to see the relationship between the energy matrices

$$B_{\mu\nu}=(a_\mu\mid F\mid a_\nu)$$

$$=[\sum_\gamma (1+S)_{\gamma\mu}{}^{-\frac{1}{2}}\phi_\gamma{}^*\mid F\mid \sum_\delta (1+S)_{\nu\delta}{}^{-\frac{1}{2}}\phi_\delta]$$

$$=\sum_\gamma\sum_\delta (1+S)_{\gamma\mu}{}^{-\frac{1}{2}}(1+S)_{\nu\delta}{}^{-\frac{1}{2}}(\phi_\gamma{}^*\mid F\mid\phi_\delta). \qquad \text{(AI.8)}$$

Define the atomic function matrix as

$$\mathcal{H}_{\gamma\delta}=(\phi_\gamma{}^*\mid F\mid\phi_\delta)=\mathcal{H}_{\delta\gamma}, \qquad \text{(AI.9)}$$

$$B_{\mu\nu}=\sum_\gamma\sum_\delta (1+S)_{\gamma\mu}{}^{-\frac{1}{2}}(1+S)_{\nu\delta}{}^{-\frac{1}{2}}\mathcal{H}_{\gamma\delta}$$

$$=\sum_\gamma (1+S)_{\gamma\mu}{}^{-\frac{1}{2}}[(\mathbf{1}+\mathbf{S})^{-\frac{1}{2}}\boldsymbol{\mathcal{H}}]_{\nu\gamma}$$

$$=[(\mathbf{1}+\mathbf{S})^{-\frac{1}{2}}\boldsymbol{\mathcal{H}}(\mathbf{1}+\mathbf{S})^{-\frac{1}{2}}]_{\mu\nu}, \qquad \text{(AI.10)}$$

$$\mathbf{B}=(\mathbf{1}+\mathbf{S})^{-\frac{1}{2}}\boldsymbol{\mathcal{H}}(\mathbf{1}+\mathbf{S})^{-\frac{1}{2}}, \qquad \text{(AI.11)}$$

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[26] P.-O. Löwdin, J. Chem. Phys. **18**, 365 (1950). In Löwdin's derivation the definition of the overlap matrix element is $S_{\mu\nu}=\int\phi_\mu{}^*\phi_\nu d\tau-\delta_{\mu\nu}$. This is not the convention followed in expressions involving the overlap matrix in Eqs. (38)–(40) of this paper. Here the overlap matrix element does not contain the $\delta_{\mu\nu}$ term.

TABLE XIII. Test of approximation $\langle\overline{Aa}\mid Ta+C_{Ia}+U_{Ia}+X_{Ia}\mid 2s\rangle=\langle Aa\mid 2S\rangle E_{2s}$.

R[a]	$\langle\overline{Aa}\mid 2s\rangle$	$\langle T\rangle$[b]	$\langle V_c\rangle$[c]	$\langle V_{ex}\rangle$[d]	$\langle E\rangle$[e]	$\{\langle E\rangle/\langle\overline{Aa}\mid 2s\rangle\}$[f]
5.2467	0.1095	0.1026	−4.2917	−0.5740	−4.7631	−43.52
6.0000	0.0787	0.0062	−3.1350	−0.4124	−3.5412	−44.98
8.0000	0.0286	−0.0501	−1.1047	−0.1484	−1.3032	−45.59

[a] Separation measured in a_0 (Bohr radii).
[b] $\langle T\rangle=\langle\overline{Aa}\mid Ta\mid 2s\rangle$, all energies in electron volts.
[c] $\langle V_c\rangle=\langle Aa\mid U_{Ia}+C_{Ia}\mid 2s\rangle$.
[d] $\langle V_{ex}\rangle=\langle Aa\mid X_{Ia}(Aa,2s)\mid 2s\rangle$.
[e] $\langle E\rangle=\langle T\rangle+\langle V_c\rangle+\langle V_{ex}\rangle$.
[f] If the approximation were exact, this value would be $E_{2s}=-47.15$ eV.

and therefore the two equations can be written in the form

$$\mathbf{Bx}=\epsilon\mathbf{1x}, \tag{AI.12}$$

$$\mathfrak{H}\mathbf{y}=\epsilon'(\mathbf{1}+\mathbf{S})\mathbf{y}, \tag{AI.13}$$

$$(\mathbf{1}+\mathbf{S})^{-1}\mathfrak{H}\mathbf{y}=\mathbf{1y}\epsilon. \tag{AI.14}$$

Multiply on the left by $(\mathbf{1}+\mathbf{S})^{\frac{1}{2}}$:

$$(\mathbf{1}+\mathbf{S})^{-\frac{1}{2}}\mathfrak{H}\mathbf{y}=\mathbf{1}(\mathbf{1}+\mathbf{S})^{\frac{1}{2}}\mathbf{y}\epsilon', \tag{AI.15}$$

$$(\mathbf{1}+\mathbf{S})^{-\frac{1}{2}}\mathfrak{H}(\mathbf{1}+\mathbf{S})^{-\frac{1}{2}}(\mathbf{1}+\mathbf{S})^{\frac{1}{2}}\mathbf{y}=\mathbf{1}(\mathbf{1}+\mathbf{S})^{\frac{1}{2}}\mathbf{y}\epsilon', \tag{AI.16}$$

$$\mathbf{B}(\mathbf{1}+\mathbf{S})^{\frac{1}{2}}\mathbf{y}=\mathbf{1}(\mathbf{1}+\mathbf{S})^{\frac{1}{2}}\mathbf{y}\epsilon', \tag{AI.17}$$

$$\therefore\quad \epsilon'=\epsilon,$$

$$(\mathbf{1}+\mathbf{S})^{\frac{1}{2}}\mathbf{y}=\mathbf{x}, \tag{AI.18}$$

so that the SCF vectors are simply connected in the two representations.

APPENDIX II. COMMENTS ON THE APPROXIMATIONS AND CALCULATIONS

A. The Integral $\langle\overline{Aa}\mid Ta+U_{Ia}+C_{Ia}+X_{Ia}\mid Ii\rangle$

Throughout this work the approximation has been made that

$$\langle\overline{Aa}\mid Ta+U_{Ia}+C_{Ia}+X_{Ia}(\overline{Aa},\overline{Nn})\mid Ii\rangle \approx\langle\overline{Aa}\mid Ii\rangle E_{Ii}. \tag{AII.1}$$

Terms due to this approximation play an important role in the calculation of the energy of the first excited state of neon in the crystalline state (see for example I_B). A direct test of this approximation was made for the function $\mid 2s\rangle$ for three arbitrary separations. The individual terms are displayed in Table XIII. The term in the last column should be compared to E_{2s} which is −47.15 eV for the SCF functions we used. It should be noted that one of the terms in the exchange potential cancels a term in the Coulombic potential leaving a net positive charge. It is seen from Table VIII that this approximation is good within 3%–5% at the important distances in this calculation.

B. Effect of Adding Nodes to the $\langle\overline{Aa}|$, $\langle\overline{Nn}|$ Functions

As mentioned in Sec. III most calculations were carried out using a nodeless Slater fit to the $3s$ neon excited-state function. This approximation is quite good for certain integrals and very bad for others. It is a very poor approximation for integrals such as

$$\langle\overline{Nn}\mid U_{Na}+C_{Na}\mid\overline{Mn}\rangle \tag{AII.2}$$

or

$$\langle\overline{Nn}\mid U_{Aa}+C_{Aa}'\mid\overline{Aa}\rangle. \tag{AII.3}$$

In the first integral the behavior of the charge density $\varphi_{Nn}\varphi_{Mn}$ in the immediate vicinity of the Nth nucleus determines the sign and magnitude of the integral while in the second integral a long range interaction, $-\mid R_A-r\mid^{-1}$, makes the value less sensitive to the addition of nodes. In Table XIV the effect on the first integral of orthogonalizing the Slater fit to the SCF neon ground-state functions is displayed. In Table XV the change in the second integral due to the addition of nodes is shown. In Table XVI the overlap integrals $\langle\overline{Nn}\mid\overline{Mn}\rangle$ are indicated for the $\langle\overline{Nn}|$, $\langle\overline{Mn}|$ orthogonalized. All the above demonstrate that care must be used in the use of an analytic fit to a wavefunction in calculations of this nature.

TABLE XIV. Effect of nodes on the integral $\langle Nn\mid U_{Na}+C_{Na}\mid Mn\rangle$.

R	$\langle\overline{Nn}|$, $\langle\overline{Mn}|$[a]	$\langle\overline{Nn}^*|$, $\langle\overline{Mn}|$[a]	$\langle\overline{Nn}^*|$, $\langle\overline{Mn}^*|$[a]
6.000	−0.090	0.1824	0.1850

[a] For Tables XIV–XVI *only* $\langle\overline{Nn}^*|$ denotes the Slater fit with nodes added; $\langle\overline{Nn}|$ a nodeless Slater fit. All energies in eV.

TABLE XV. Effect of nodes on the integral $\langle\overline{Nn}\mid U_{Aa}+C_{Aa}\mid\overline{Aa}\rangle$ (in electron volts).

R	$\langle\overline{Nn}\mid U_{Aa}+C'_{Aa}\mid\overline{Aa}\rangle$	$\langle\overline{Nn}^*\mid U_{Aa}+C'_{Aa}\mid\overline{Aa}^*\rangle$
5.8124	−3.5948	−3.0079
8.2200	···	−1.5152
10.0674	···	−0.7550

TABLE XVI. Effect of nodes on overlap of analytic fit to excited state.

R	$\langle \overline{Nn}^* \mid \overline{Mn}^* \rangle$	$\langle \overline{Nn} \mid \overline{Mn} \rangle$
5.0	0.6024	0.6257
5.5	0.5519	0.5693
6.0	0.5009	0.5133
6.5	0.4500	0.4584
7.0	0.4003	0.4055

C. Comparison of the Mulliken Approximation to Exact Three-Center Integrations

A very important approximation made throughout this calculation is expressed by Eq. (33) and makes possible an estimate of certain three-center integrals as a properly weighted sum of two-center integrals. The Mulliken approximation has been checked many times and found to lead to reasonable agreement with exact integrations. Before using the Mulliken approximation for this calculation comparison was made to the integral $\langle \overline{Nn} \mid U_{Aa}+C_{Aa}' \mid \overline{Mn} \rangle$ where $\langle \overline{Nn} \mid$ and $\langle \overline{Mn} \mid$ lay on a straight line bisected by the Ath nucleus. Table XVII gives this comparison. One sees that the agreement is remarkably good for this case, which would be thought to be difficult due to the small overlap of these functions (~0.1–0.06) and the rapid variation of the potential over the region.

While this comparison in no way validates the use of the Mulliken approximation for other integrals such as $\langle \overline{Nn} \mid U_{Ia}+C_{Ia} \mid \overline{Mn} \rangle$, it does increase the confidence that a reasonable estimate of such integrals is obtained. The Mulliken approximation calculations probably follow closely the behavior of the exact integrations when the lattice parameter is varied or new charge transfer states are added to the basis set even if the magnitudes of the integrals are in error.

D. Ground-State Energy Shifts and Ground-State Neon Functions

Throughout this calculation it has been assumed that the ground-state functions suffer negligible energy change in the solid state. Also, use has been made of a very small basis set SCF function to represent the charge density of a neon atom. For the kinds of integrals dealt with here this approximation is not serious in the individual integrals, but the rather large sums of these integrals tend to magnify these errors. Thus the uncertainty in the final orbital energy could easily be 1–2 eV due to the use of these neon functions. Comparison of terms calculated by us for the case of an argon impurity in a neon crystal (to be published) with the calculation done previously by Gold[10] leads us to believe that this error is in the positive direction, such that a 1–1½ eV blue shift is within the uncertainty of this calculation. However the use of these neon functions would be completely erroneous for a ground state calculation. This is most easily demonstrated by the overlap of a $2p$ neon function with other ground state functions using a minimal basis set ($E_{2p}=-0.56199$ a.u., the set used for this calculation) and a nominal basis set ($E_{2p}=-0.84973$), it is seen from Table XVIII that a difference of orders of magnitude results in the ground-state overlap.

TABLE XVII. Comparison of Mulliken approximation and exact numerical integration.

R[a]	exact[b]	Mulliken approx.[b]
10.6248	−0.9144	−0.7267
11.6248	−0.4547	−0.4377
12.6248	−0.2232	−0.2868

[a] $R=|\mathbf{R}_M-\mathbf{R}_N|$ in a_0.

[b] Energy in electron volts for integral $\langle \overline{Nn} \mid U_{Aa}+C_{Aa}' \mid \overline{Mn} \rangle$ mentioned in the text.

TABLE XVIII. Comparison of ground state overlap for a minimal and normal basis set $2p_{Ne}$ function.

R	$S(2p\sigma, 2p\sigma)$ nominal	$S(2p\sigma, 2p\sigma)$ minimal	$S(2p\sigma, 2s)$ nominal	$S(2p\sigma, 2s)$ minimal
5.8124	0.001295	0.000024	0.003114	0.000207
8.22	0.000041	0.000000	0.000086	0.000001

Using the E_{Ii} and overlap values for the nominal basis set would lead to an orthogonalization energy increase (i.e., I_B) of the order 0.006 eV for a ground-state $2p$ function. The penetration integrals and so on are expected to be of the same order of magnitude but of opposite sign. Thus the polarization energies and other relatively weak interactions are at least as important as the orthogonalization and penetration effects and it would be inconsistent to include them for the ground state and not the excited state. In any case the energy shift of the ground state is most certainly small compared to the computational uncertainties of the individual terms that make up the net energy shift of the excited state.

E. Details of Calculation

In this section some of the more detailed results of the calculation are presented in order that the reader may have a better understanding of the interaction of a diffuse excited state with the crystal environment.

TABLE XIX. Effects of orthogonalization.

Lattice constant	η_A[a]	Effect of nodes[b]	Effect of nodes at[c] First shell	Second shell	Third shell
3.71	0.8219	9.307	···	···	···
4.11	0.8928	5.517	4.990	0.501	0.026
4.51	0.9370	3.198	···	···	···

[a] $\eta_A=[1-\sum_{Ii}\langle Aa \mid Ii \rangle^2]$.

[b] The value in electron volts of $-\sum_{Ii}\langle Aa \mid Ii \rangle^2 E_{Ii}$ where the sum over Ii extends over the first three shells (42 atoms).

[c] The value in electron volts of $\sum_{Ii}\langle Aa \mid Ii \rangle^2 E_{Ii}$ where the sum is over the atoms of only the first, second, or third shell (at 5.8124, 8.22, 10.0674 a_0, respectively, for the case evaluated).

TABLE XX. Values of Coulomb and exchange potentials and overlap integrals at various distances.

	Separation[a]	Total Coulomb[b]	Total exchange[c]	$s(1s, 3s)$	$s(2s, 3s)$	$s(2p\sigma, 3s)$
	5.247	−0.180	−0.295	0.0115	0.1080	0.0351
1	5.812	−0.127	−0.184	0.0089	0.0870	0.0302
	6.378	−0.075	−0.113	0.0069	0.0690	0.0251
	7.420	−0.025	−0.043	0.0038	0.0380	0.0164
2	8.220	−0.008	−0.015	0.0025	0.0250	0.0111
	9.02	0.000	−0.005	0.0013	0.0130	0.0071
	9.0876	0.000	−0.004	0.0012	0.0120	0.0070
3	10.067	0.000	0.000	0.0008	0.0080	0.0041
	11.047	0.000	0.000	0.0002	0.0020	0.0025

[a] Nuclear separation on Bohr radii. The groups of three are the separations of the first, second, and third shells, respectively, with the values in the bracket being for the various lattice constants taken.

[b] Value in electron volts of $\langle \overline{Aa} \mid U_{Ia}+C_{Ia} \mid \overline{Aa} \rangle$.

[c] Value in electron volts of $\langle Aa \mid X_{Ia}(\overline{Aa}, \overline{Aa}) \mid Aa \rangle$.

In Table XIX is presented the normalization constant $\eta_A(=\eta_N)$ for the various lattice parameters. Also there is displayed in Table XIX the effect of orthogonalization of the 3*s* function to the first-, second-, and third-shell atoms. It is seen that nearly all of the I_B term is due to the first shell. Roughly the same would be true for the penetration energy, I_C. Thus Table XIX supports the statement that the energy of the first excited neon state is determined by the details of the wavefunction in the vicinity of the first-shell atoms.

In Table XX are presented values of the total Coulombic and penetration integrals vs distance. Also some typical overlap values appears which show the importance of the first shell relative to the other shells. One also should note that the value of $S(2s, 3s)$ is roughly thirty times that of $S(2p\sigma, 2s)$ using the nominal basis set for both $2p\sigma$ and 2*s* functions.

APPENDIX III. EXCITON SHIFT

In the calculation of the matrix element H_{11} we have not included the exciton bandwidth. The electromagnetic coupling between the atoms of the crystal gives rise to an additional energy shift arising from the lifting of the degeneracy due to the translational symmetry of the solid. A suitable framework with which to estimate the (neutral) singlet exciton bandwidth in neon is provided by the work of Frenkel and Davydov. Their analysis starts from the tight-binding approximation in the Heitler–London scheme. The wavefunctions ${}^{1,3}\phi_e$ do not diagonalize the tight binding crystal Hamiltonian because of the existence of interatomic interactions; the energy correction is given in the form[3]

$$\mathcal{E}_{\text{exc}}=\sum_{I\neq J} E_{IJ} \exp[i\mathbf{k}\cdot(\mathbf{R}_J-\mathbf{R}_I)], \qquad \text{(AIII.1)}$$

where the off-diagonal excitation transfer matrix elements are given by

$$E_{IJ}=(\psi_e^I \mid H \mid \psi_e^J), \qquad \text{(AIII.2)}$$

with ψ_e^I and ψ_e^J singly excited states of the crystal with the excitation located on Atoms I and J, respectively, and $\mathbf{k}$ is the reciprocal wave vector, whose values are limited within the first Brillouin zone.

For the case of cubic symmetry, when Jahn–Teller distortions are disregarded, we can assume that the degeneracy of the excited P state is maintained in the lattice. Applying the multipole expansion and neglecting exchange effects, $\mathcal{E}_{\text{exc}}$ can be approximated by dipole–dipole interaction term

$$\mathcal{E}_{\text{exc}}=-\mid \boldsymbol{\mu} \mid^2 \times\sum_{I\neq J}\left\{3 \cos^2\left[\frac{\boldsymbol{\mu}\cdot(\mathbf{R}_I-\mathbf{R}_J)}{\mid \boldsymbol{\mu} \mid \mid \mathbf{R}_I-\mathbf{R}_J \mid}\right]-1\right\} \Big/ \mid \mathbf{R}_I-\mathbf{R}_J \mid^3, \qquad \text{(AIII.3)}$$

where $\boldsymbol{\mu}$ is the transition dipole moment. This expression is adequate for the singlet–singlet transition. The dipole moment $\boldsymbol{\mu}$ has the same magnitude and direction for all atoms. For the case of an optical transition, $\mathbf{k}\approx 0$ (i.e., $\mathbf{k}$ is of the order of $2\pi/\lambda$), and the dipole summation has to be carried out over the whole lattice. The summation can now be replaced by an integral leading to the result

$$\mathcal{E}_{\text{exc}}=(8\pi/3V) \mid \boldsymbol{\mu} \mid^2 P_2[\cos(\boldsymbol{\mu}\cdot\mathbf{k})] \times\{ j_0(\mid \mathbf{k} \mid R_0)+j_2(\mid \mathbf{k} \mid R_0)\}, \qquad \text{(AIII.4)}$$

where P_2 is the Legendre polynomial of order 2, j_0 and j_2 are spherical Bessel functions, V and R_0 are the mean volume and radius per atom, respectively, so that $V=(4\pi/3)R_0^3$. When the exciton is created by light, $(\boldsymbol{\mu}\cdot\mathbf{k})=\pi/2$ so that $P_2[\cos(\boldsymbol{\mu}\cdot\mathbf{k})]=-\frac{1}{2}$. Furthermore, as $\mid \mathbf{k} \mid R_0 \ll 1$, $j_0(\mid \mathbf{k} \mid R_0)+j_2(\mid \mathbf{k} \mid R_0)\approx 1$, and

$$\mathcal{E}_{\text{exc}}\approx-\mid \mu \mid^2/R_0^3. \qquad \text{(AIII.5)}$$

For an oscillator strength of 0.1 for Ne, the transition dipole moment is 1.4×10^{-18} cm·esu. Setting $R_0=2.0$ Å, we find that $\mathcal{E}_{\text{exc}}=-0.26$ eV. This contribution, due to the exciton bandwidth, is relatively small.