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NMR Study of Molecular Configuration and Order in a Fluorinated-Liquid-Crystalline Schiff Base*

N. BRAVO AND J. W. DOANE

Department of Physics and Liquid Crystal Institute, Kent State University, Kent, Ohio

AND

S. L. Arora and J. L. Fergason Liquid Crystal Institute, Kent State University, Kent, Ohio 44240 (Received 13 September 1968)

The fluorine and proton spin resonances in the nematic-liquid-crystal state of terephthalbis(aminofluorobenzene) are studied using the method of moments. The second moment of the proton line has a large dependence on the molecular configuration as well as on the degree of molecular order. The fluorine second moment, on the other hand, has a negligible dependence on the configuration and is used to obtain a measure of the order. With the degree of order known, the second moment of the proton resonance is used to examine possible configurations the molecule may follow. The results rule out the possibility of a planar molecule as well as a molecule in which the aromatic rings and the -N=CH- linkage groups are allowed to rotate around their bonds in an unhindered fashion. Best agreement with the data is found for the case where the plane containing the linkage group makes a preferred angle near 20° relative to the plane of the terminal aromatic rings. The temperature dependence of the proton spectrum is also interpreted in terms of the molecular order.

I. INTRODUCTION

One of the most striking illustrations of the molecular order exhibited by nematic-liquid-crystal systems is the broad NMR spectrum that these systems show. The first reported NMR study in nematic liquid crystals was that of Spence¹ and his co-workers, who observed this spectrum in para-azoxyanisole as a broad resonance line, similar to that seen in solids. Since then several NMR workers have made more detailed studies using the method of moments,² electric-field effects on NMR spectra,³ selective deuteration to study the quadrupolar as well as the simplified proton spectra,⁴ and high resolution^{5,6} to include that on molecules dissolved in liquid crystals.

The work reported here uses the second moment to study the proton and fluorine resonance in the nematic phase of terephthalbis $(4-aminofluorobenzene)^7$ shown in Fig. 1. This compound belongs to a Schiff base series. It is of interest because the line shape or second moment of the fluorine resonance in the nematic phase does not depend on the molecular configuration, or more specifically, on the relative arrangement or motion of the terminal aromatic rings and the imine linkage groups which make up the molecule. Considerable confusion exists in the literature⁸⁻¹⁰ as to what configuration such

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^a E. F. Carr, E. A. Hoar, and W. T. MacDonald, J. Chem. Phys. 48, 2822 (1968).
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 ¹⁰ G. Favini and A. Gamba, J. Chim. Phys. **62**, 995 (1965).

a molecule will follow. From the fluorine resonance the degree of molecular order can be obtained free from uncertainties in the arrangement or motion of the groups of the molecule. The proton resonance does, on the other hand, depend on the molecular configuration as well as the order. Knowing the degree of order from the fluorine resonance, the proton resonance is studied and its second moment is calculated for various rigid arrangements as well as for cases where the groups reorient relative to one another. A measurement of the proton second moment is then used to determine possible configurations.

II. CALCULATION OF THE SECOND MOMENT

A. Fluorine Spins

Unlike the resonance lines observed in the solid state, the NMR spectrum or shape of the broad line in the liquid-crystalline state is determined only by the interacting spins within the molecule. The intermolecular magnetic dipole interactions are averaged to zero due to rapid translational diffusion of the molecules in the nematic liquid crystal. The fact that a broad spectrum exists at all is a consequence of the order exhibited by the elongated molecules which, in the compounds reported here, tend to align, on the average, with their long axis in the direction of the magnetic field. The magnetic-dipole interactions of the spins in the molecule do not therefore average to zero. There is not perfect alignment however and the width of the spectrum is less than one would expect with the same molecular order characteristic of a crystalline solid. The molecules which show liquid crystallinity usually contain several proton spins. As a consequence there exists a multiplicity of spin states which generally appear as a single broad line with some structure superimposed or under high resolution as a complex spectrum of lines.

As in the case of solids the resonance line can be

¹ R. D. Spence, H. A. Moses, and P. L. Jain, J. Chem. Phys. **21**, 380 (1953).

studied by the method of moments.¹¹ This work makes use of the second moment defined by

$$\langle \Delta H^2 \rangle = \left(\int_0^\infty \left(H - \langle H \rangle \right)^2 f(H) \, dH \, \middle/ \, \int_0^\infty f(H) \, dH \right), \tag{1}$$

where f(H) describes the shape of the resonance line and H is the magnetic field at which resonance occurs. The theoretical second moment in liquid crystals² is an average of that originally calculated by Van Vleck for crystalline solids which is expressed as

$$\begin{split} \langle \Delta H^2 \rangle &= a N^{-1} \sum_{jk} \langle (3 \cos^2 \theta_{jk} - 1) / \mathbf{r}_{jk}^3 \rangle^2 \\ &+ b N^{-1} \sum_{jf} \langle (3 \cos^2 \theta_{jf} - 1 / \mathbf{r}_{jf}^3) \rangle^2. \end{split}$$
(2)

The first term in the expression is for the case where the interacting nuclear dipole of spin I and gyromagnetic ratio γ is of the same species as the observed nuclear spin. In this term r_{jk} is the internuclear distance between spins j and k; θ_{jk} is the angle between the direction of the vector r_{jk} and the direction of the applied-magnetic field; N is the number of nuclei per unit volume; and $a = \frac{3}{4}\gamma^2 \hbar^2 I(I+1)$. The second term in the expression takes into account nuclear spins of a different species which possess a spin I_f and gyromagnetic ratio γ_f in which case $b = \frac{1}{3}\gamma_f^2 \hbar^2 I_f(I_f+1)$.

The average of Eq. (2) in the case of liquid crystals has been calculated by Weber.² Following Weber we have assumed that the molecular order can be represented as a scalar and have expressed this average as

$$\langle (3\cos^2\theta_{jk}-1)/r_{jk}^3 \rangle = \langle (\frac{3}{2}\cos^2\gamma_{jk}-\frac{1}{2})/r_{jk}^3 \rangle (\frac{3}{2}\cos^2\phi-\frac{1}{2}) \\ \times (\frac{3}{2}\cos^2\xi-\frac{1}{2}) (3\cos^2\theta_0-1).$$
(3)

In the molecular system diagrammed in Fig. 1 γ_{jk} represents the angle between r_{jk} and the *para* axis of the molecule. We have retained the average brackets around the first term on the right side of the equation since r and γ may vary in time. The angle ϕ is the angle between *para* axis and the molecular axis. The molecule in Fig. 1 is diagrammed in the *trans* configuration in which case $\phi = 11^\circ$. One might also expect the molecule



FIG. 1. The axes and direction of preferential orientation relative to the applied magnetic field of the molecule terephthalbis(4-aminofluorobenzene).

¹¹ J. H. Van Vleck, Phys. Rev. 74, 1168 (1948).

TABLE I. Band lengths used in the second moment calculation for terephthalbis(p-aminofluorobenzene).

Bond	Nuclear distance (Å)
C _{ar} -C _{ar}	1.40
C _{sr} -H _{ar}	1.08
C _{ar} -F	1.30
C _{ar} -N	1.44
N=C	1.27
С-Н	1.08

to form a *cis* configuration where $\phi = 0^{\circ}$. The term $(\frac{3}{2}\cos^2\xi - \frac{1}{2})$ is the degree of order, *S*, of the molecule where ξ represents the angle created by thermal oscillation of the molecular axis; θ_0 represents the angle between the magnetic field and direction about which the molecule is preferentially oriented. In this case θ_0 was taken to be zero; i.e., it was assumed that the molecular axis oscillates about the direction of the magnetic field.

Due to the large separation between the fluorine spins in the system in Fig. 1 the only spins which effect the second moment of fluorine are protons spins and hence only the second term in Eq. (2) need be used in the calculation. The only protons that need be considered in the calculation are those in the fluorobenzene rings and the proton in the -N=CH- linkage that links the aromatic rings to which the fluorine is attached. The protons in the central benzene ring are greater than 7 Å distant from the fluorine and contribute only to a negligible extent. It is important to note that because of the para position of the fluorine, the fluorine second moment calculation is independent of any possible molecular configuration. That is, r and γ will not vary for those protons which have a measurable effect on the second moment. Because of the single bond between the benzene rings and the imine linkage group one might expect a rotation of the fluorobenzene ring relative to the imine linkage about this bond, but such a rotation will not alter r or γ in the calculation. The second moment can then be computed using Eqs. (2) and (3) with the only unknown quantity being S, the ordering parameter. A measurement of the fluorine second moment should then yield a value for S. The intranuclear distances were determined from the bond lengths¹² in Table I. The bond angles relative to the para axis were taken either as 60° or 0° as indicated in Fig. 1.

B. Proton Spins

The second moment for the protons does depend on the molecular configuration. Here the first term in Eq. (2) is of importance. If the molecule is not a rigid structure but reorientation among the various groups

¹²L. E. Sutton (Ed.), Chem. Soc. (London) Spec. Publ. 11 (1958).



FIG. 2. The parameters used to describe the position of nuclear spin j relative to spin i.

of the molecule should occur, an average of the first term on the right-hand side of Eq. (3) must be calculated. For example consider the molecule in Fig. 1 where benzene rings may rotate with respect to the imine linkage groups. Unlike the case for fluorine, the intranuclear distance r between the proton spin in the imine group and any spin in the benzene ring would vary with time as would the angle γ . We therefore found it convenient to make a change of variables according to Fig. 2 and write

$$(3\cos^2\gamma - 1)/r^3 = 3B^2/(\alpha - \beta \cos\Omega)^{5/2} - (\alpha - \beta \cos\Omega)^{-3/2},$$
 (4)

where $\alpha = A^2 + B^2 + R^2$ and $\beta = 2AR$. When considering only the spins within the benzene ring, Ω is of course fixed. If the entire molecule is rigid, that is if no reorientation occurs between the various groups of the molecule relative to one another, then Ω is also fixed for all interacting spins. If, however, reorientation does occur, then Ω varies with time. If the frequency, ν_c , of reorientation is large compared to the linewidth, δv , produced by a fixed or rigid system then the average of Eq. (4) can be calculated. The average, however, depends on the manner of reorientation. Two types of motion were considered; a uniform rotation of the linkage groups relative to the benzene ring and a flipping motion in which the end aromatic rings were considered to remain at some preferred orientation relative to the imine groups for a time which is long compared to the time spent in reorientation. If uniform motion is considered the average of Eq. (4) is

$$\frac{1}{2\pi}\int_0^{2\pi} \left[\frac{3B^2}{(\alpha-\beta\cos\Omega)^{5/2}} - \frac{1}{(\alpha-\beta\cos\Omega)^{3/2}}\right]d\Omega.$$
 (5)

The above definite integral can be expressed as

$$\frac{B^2}{\pi(\alpha^2 - \beta^2)} \left\{ \frac{8\alpha(\alpha + \beta)^{1/2}}{\alpha^2 - \beta^2} E\left[\left(\frac{2\beta}{\alpha + \beta} \right)^{1/2} \right] - \frac{2}{(\alpha + \beta)^{1/2}} \\ \times K\left[\left(\frac{2\beta}{\alpha + \beta} \right)^{1/2} \right] \right\} - \frac{(2/\pi)(\alpha + \beta)^{1/2}}{(\alpha^2 - \beta^2)} E\left[\left(\frac{2\beta}{\alpha + \beta} \right)^{1/2} \right], \quad (6)$$

where $E\{[2\beta/(\alpha+\beta)]^{1/2}\}$ and $K\{[2\beta/(\alpha+\beta)]^{1/2}\}$ are elliptic integrals of the first and second kind, respectively. The average of Eq. (4) for the flipping motion can be calculated by averaging the preferred orientations.

Using a value of S as determined from the measurement of the second moment for fluorine, the second moment for the protons can be calculated for various rigid configurations using Eqs. (2)-(4). If reorientation occurs then the appropriate average of Eq. (4) must be used. The calculated values, along with the measured second moment, are listed in a later section.

III. EXPERIMENTAL DETAILS

A. Apparatus and Samples

The data were acquired using a Pound-Watkins marginal oscillator¹³ and a conventional lock-in system. The temperature of the samples was maintained in two different ways. Where variable temperatures were needed to determine the temperature dependence of the NMR spectrum, a gas-flow system, Varian Model V-4557, was used. For the detailed second moment work an improvement was made in the temperature homogeneity by constructing a small oven enclosing the sample and the spectrometer rf coil. The oven was suspended in a Dewar flask which was, in turn, placed in the magnetic field. In this case the temperature homogeneity was checked by observing the change in appearance of the liquid crystal at the nematicisotropic point. The temperature gradient was found to be nearly 5° at 225°C in the gas-flow system but better than 0.5°C in the oven. The samples were placed in an evacuated glass tube and inserted into the rf coil located in the oven. The temperature of the sample was measured by a thermocouple immersed in the liquid crystal.

Terephthalbis(4-aminofluorobenzene) was prepared by refluxing 4-fluoroaniline (2M) and terephthalaldehyde (1M) in absolute alcohol for 5-6 h. The product was isolated and recrystallized several times from benzene. C-N: 151°C; N-L: 225°C (C=crystal; N=nematic; L=liquid). Transition temperatures were determined by the melting-point capillary-tube method, optical studies and DTA (differential thermal analysis). Figure 3 shows the endo- and exothermograms for this compound determined by a DuPont 900 DTA.

Terephthalbis(2-amino-5-chloropyridine) was prepared similarly by refluxing 2-amino-5-chloropyridine (2M) and terephthalaldehyde (1M) in absolute alcohol. The product after isolation was recrystallized several times from chloroform. C-N: 259°; N-L: 289°.

Analysis: calculated for $C_{18}H_{12}N_2Cl_2$; N, 15.77. Found: N, 15.74.

Bis(4-chlorophenyl) terephthalate was prepared by the dropwise addition of terephthaloyl chloride (1M)

¹³ G. D. Watkins, Ph.D. thesis, Harvard University, Cambridge Mass., 1952.



in dry toluene to 4-chlorophenol (2M) also in toluene and in the presence of anhydrous pyridine (2M). After the addition the reaction mixture was refluxed for 24 h, filtered hot to remove the precipitated pyridine hydrochloride and the filtrate allowed to cool. The product after isolation was recrystallized several times from chlorobenzene. C-N: 196°; N-L: 226°.



for (a) fluorine, and (b) protons in terephthalbis(4-aminofluorobenzene) in the nematic-liquid-crystal phase. Both recordings were taken at the same temperature of 163°C.

B. Data and Results

The fluorine resonance in terephthalbis(4-aminofluorobenzene) is shown in Fig. 4(a). A number of such traces were taken, all at the same temperature of 163° but at different magnitudes of the modulation field. When corrected for modulation,¹⁴ the value for the second moment for fluorine was measured to be $2.70\pm$ 0.10×10^{-2} G². Using Eqs. (2) and (3) the second moment was calculated to be $8.60\times10^{-2}(\frac{3}{2}\cos^2\phi-\frac{1}{2})^2S^2$ in units of G².

The proton resonance line for the same compound and at the same temperature of 163° is given in Figure 4(b). The second moment for this line was measured to be 3.03 ± 0.10 G². Using the value 2.70/8.60 for the terms $S^2(\frac{3}{2}\cos^2\phi-\frac{1}{2})^2$, obtained from the fluorine line, the theoretical values for the second moment of the proton spectrum are calculated as described in Sec. II (see Table II). The values based on a rigid molecule are given starting with the planar configuration in which the plane containing the -N=CH- linkage makes a fixed angle $\Omega = 0$ with respect to the plane of the benzene rings as diagrammed in Fig. 1. Values for the second moment are then listed for discrete values of Ω as the plane containing the imine linkage is rotated out of the plane containing the aromatic-ring groups. Although the values of $\langle \Delta H^2 \rangle$ are given for the case where three rings lie in the same plane, a rotation of the central ring out of this plane has little influence on the calculated second moment compared to the relative positioning of an end ring and the associated linkage group. The values based on a reorienting model are given first for the free or uniform rotation of the aromatic rings relative to the linkage groups. In this case all the molecular groups are considered to reorient in an unhindered fashion, at the frequency $\nu_c > \delta \nu$.

The second case is calculated for the end rings ¹⁴ E. R. Andrew, Phys. Rev. 91, 425 (1953).

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FIG. 5. Absorption curve for the proton spins obtained by integrating the experimental derivative in Fig. 4(b).

alternating or flipping between various preferred positions. For example, the second case listed in Table II is the case where the end rings flip out of and back into the planar configuration diagrammed in Fig. 1. In this case the plane containing the terminal rings flip 180° at a rate which is fast compared to the time spent in the preferred planar configuration.





FIG. 6. The molecule bis(4-chlorophenyl) terephthalate, together with its proton absorption derivative in the nematicliquid-crystal phase.

As mentioned earlier, there is an uncertainty in the value of ϕ , i.e., whether ϕ should be 11° or 0° corresponding to the *trans* or *cis* configuration with respect to the benzene rings. This uncertainty has no effect on the above results pertaining to the configuration of the end aromatic rings and their linkage groups due to the fact that the term $(\frac{3}{2}\cos^2\phi - \frac{1}{2})$ is canceled when the results of the fluorine second moment are combined with the calculated values for the proton second moment. In this work it was not possible to determine which of the two configurations (*trans* or *cis*) existed.

The two satellites appearing in the proton line have been assigned to the *ortho* aromatic protons identified as H_2 and H_3 as well as H_5 and H_6 in Fig. 1. The absorption curve obtained by integrating the proton spectrum is given in Fig. 5. The broad central portion is attributed



FIG. 7. The molecule terephthalbis (2-amino-5-chloropyridine) together with its proton absorption derivative in the nematic-liquid-crystal phase.

to the proton in the imine group. The very small narrow line in the center could not be assigned to a site in the molecule. Its amplitude was constant with large variations in temperature, except very near the nematicisotropic transition.

The validity of the above assignments can be seen by the recorded proton derivative in Fig. 6 of bis(4chlorophenyl) terephthalate. Here the imine linkage has been replaced by an ester linkage containing only nuclei of spin zero in which case the central portion of the line is absent.

An additional verification is seen in Fig. 7 which shows a recording of the proton resonance in terephthalbis(2-amino-5-chloropyridine) where one of the ring protons has been replaced by nitrogen. The satellites are reduced in intensity while the central line increases as would be expected.

If the proton in the imine linkage in terephthal-



bis(4-aminofluorobenzene) interacts very little with the protons on the benzene rings, the degree of order can be obtained from the splitting, δH , of the satellites,⁴ from the expression

$$\delta H = 3\gamma \hbar \left[\left(\frac{3}{2} \cos^2 \gamma - \frac{1}{2}\right) / r^3 \right] \left(\frac{3}{2} \cos^2 \phi - \frac{1}{2}\right) S.$$
(7)

A direct calculation using the splitting between the satellite peaks in Fig. 5 or the crossover points in Fig. 4(b) gives S=0.66. The above value of S assumes the *trans* configuration ($\phi=11^{\circ}$). This is in disagreement with the value of S=0.58 from the fluorine second moment data that is obtained when $\phi=11^{\circ}$. The discrepancy in the S values arises from the fact that the imine proton interacts with the aromatic protons to

TABLE II. The theoretical second moment of the proton resonance vs the molecular configuration to be compared with a measured value of the second moment of 3.03 ± 0.10 G².

Molecular configuration	Calculated proton second moment for $S=0.58$
Ridged planar $\Omega = 0^{\circ}$	8.76 G ²
$\Omega = 15^{\circ}$	5.84
$\Omega = 30^{\circ}$	3.02
$\Omega = 60^{\circ}$	2.18
$\Omega = 90^{\circ}$	2.12
Reorientating uniform rotation	2.27
180° flip from $\Omega = 0$ planar configuration	5.37
Flip from a preferred angle of $\Omega = 15^{\circ}$	3.93
Flip from a preferred angle of $\Omega = 30^{\circ}$	2.57

give a larger splitting than would be obtained from the aromatic protons alone. Using the fact that the splitting is directly proportional to S where the proportionality constant is determined for the known value of S at 163°, namely 0.58, the degree order as a function of temperature can be obtained from the proton spectrum. Figure 8 shows a plot of the degree of order vs $T_{\rm red} = 100T/T_{\rm K}$, where T is the absolute temperature and $T_{\rm K}$ is the absolute temperature of the clearing point.

IV. DISCUSSION

The rigid molecule is unlikely, particularly in view of the work on some deuterated nematic structures by Phillips et al.⁴ The work on the quadrupolar deuteron spins by Phillips clearly shows rotational and oscillatory motion among the molecular groups satisfying the condition $\nu_c > \delta \nu$. Although the deuterated compounds were different than the Schiff bases used here one might also suspect reorientation among the aromatic and imine groups. On the other hand, the model in which the various groups of the molecule are uniformly rotating relative to one another is in clear disagreement with the calculated value given in Table II. One might, however, suspect a potential well causing a motion approximated by the flipping action described in the previous section. In Table II the best agreement between the calculated and measured values of the second moment is obtained when the plane of the linkage group makes an angle of 30° from the plane of the fluorinated ring for a rigid molecule. The effect of motion between the two groups is to make the agreement better at smaller angles approaching 20°.

The values for the ordering parameter given in Fig. 8 appear low.¹⁵ If the *cis* configuration is chosen $(\phi=0^{\circ})$

¹⁵ A. Saupe, Angew. Chem. Intern. Ed. Engl. 7, 97 (1968).

the values are slightly lower. A possible source of error may be the length that was used for the fluorine-carbon bond. Because of the functional dependence of the second moment on the angle γ , the second moment for fluorine is very sensitive to this particular bond. Increasing the value for the bond length has the effect of increasing the value for S determined from the fluorine second moment. For example, if a value of 1.33 Å instead of 1.30 Å is used for the bond length, the value of S changes from 0.58 to 0.60. Such a change in the order, however, would have a negligible effect on the results of the configuration studies.

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Atomic and Molecular Calculations with Pseudopotential Method. IV. Excited Atomic Valence-Electron Energy Values, Wavefunctions, and Oscillator Strengths

GEORGE MCGINN

Science Department, State University of New York, Maritime College, Fort Schuyler, Bronx, New York 10465 (Received 2 October 1968)

The pseudopotential equation of Phillips and Kleinman is solved numerically for the first six ^{2}S states, the first six ${}^{2}P^{0}$ states, and the first five or six ${}^{2}D$ states for the valence electron of the atoms Li, Na, K, Rb, Be⁺, Mg⁺, Ca⁺, Al⁺⁺, Cu, and Zn⁺. From the calculated energy values it can be seen that the polarization effect of the valence electron on systems with large cores is important even when the valence electron is in a high excited state. The integrals needed to compute the oscillator strengths for all the allowed transitions between the calculated valence states are computed.

I. INTRODUCTION

In a previous publication¹ the pseudopotential method in the Phillips and Kleinman formulation² was used to calculate the ground state and the first few excited states for a number of single valenceelectron atoms and ions. In the pseudopotential method the interaction between the core electrons and the valence electron can be written in the form of the modified potential

$$V_M = V_{\rm HF} + V_R, \tag{1.1}$$

where $V_{\rm HF}$ is the Hartree-Fock potential and V_R is the pseudopotential, which replaces the requirement that the valence-electron wavefunctions must be orthogonal to the core wavefunctions.

In the present paper the atomic calculations of Part II are extended to include higher excited states for the following atoms: Li, Na, K, Rb, Be+, Mg+, Ca+, Al++, Cu, and Zn+. For each of the atoms, the pseudowavefunctions and the orbital energy for the lowest six 2S states (including the ground state), the lowest six ${}^{2}P^{0}$ states, and the lowest five or six ${}^{2}D$ states of the valence electron were calculated. Also the integrals needed to compute the oscillator strengths for all the allowed transitions between the calculated valence states were computed.

II. THE CALCULATIONS

Let us consider an atom (or ion) with the nuclear charge Z and N electrons in closed shells plus one ¹L. Szasz and G. McGinn, J. Chem. Phys. 47, 3495 (1967),

² J. C. Phillips, Phys. Rev. 112, 685 (1958); J. C. Phillips and L. Kleinman, *ibid.* 116, 287 (1959); 118, 1153 (1960).

valence electron. Denoting the one-electron Hartree-Fock (HF) spin orbitals of the core by $\phi_1, \phi_2, \dots, \phi_N$, the solutions of the HF equations for the core spin orbitals are

$$H_{\mathbf{F}}\phi_i = E_i\phi_i \qquad (i=1,\cdots,N), \qquad (2.1)$$

where E_i is the HF orbital parameter and H_F is the HF Hamiltonian defined as

$$H_{\rm F} = -\frac{1}{2}\Delta - (Z/r) + V(g) - A(g). \qquad (2.2)$$

Here g stands for the spatial and spin coordinates, Δ is the Laplacian, and V and A are the Coulomb and exchange operators, respectively:

$$V(g) = \sum_{i=1}^{N} \int \frac{|\phi_i(g')|^2}{|\mathbf{r} - \mathbf{r}'|} \, dg', \qquad (2.3)$$

$$A(g)f(g) = \sum_{i=1}^{N} \int \frac{\phi_i(g)\phi_i^*(g')f(g')}{|\mathbf{r}-\mathbf{r}'|} \, dg'. \quad (2.4)$$

The solutions of (2.1) are held fixed throughout the rest of the calculation (the same core wavefunctions and orbital energy parameters used in Part II are used in this work), thus a "frozen" core approximation is used in this work.

Adding the valence electron to the "frozen" core we denote its pseudowavefunctions by ϕ_0 . According to Phillips and Kleinman,² ϕ_0 is the solution of the equation

where

$$(H_{\mathbf{F}}+V_{\mathbf{R}})\phi_0=E\phi_0,\qquad(2.5)$$

$$V_{R}\phi_{0} = \sum_{i=1}^{N} C_{i}(E-E_{i})\phi_{i}$$
 (2.6)