and $$\oint \frac{F^2}{[fg-(mc)^2]^{3/2}} = \frac{4\pi W}{m^3c^4}\,\frac{1}{[(l+1)\hbar - Z|e^2|/c]}$$

$$-\frac{6\pi W^3}{m^5c^8}\,\frac{(l+1)\hbar}{[(l+1)\hbar - Z|e^2|/c]^2} \; .$$

We get, therefore, by substitution of the above into Eq. (5) and after some cancellations,

$$\frac{2\pi W Z|e^2|}{c^2[(mc)^2-(W/c)^2]^{1/2}} + \hbar\pi - 2\pi$$

$$\times\left[(l+1)^2\hbar^2 - \left(\frac{Z|e^2|}{c}\right)^2\right]^{1/2} = 2\pi\hbar(n+\tfrac{1}{2}) \; . \tag{6}$$

Solving for W

$$W = mc^2 \left\{1 + \left(\frac{Z|e^2|}{\hbar c}\right)^2 \Bigg/ \left[n + \left((l+1)^2 - \left(\frac{Z|e^2|}{\hbar c}\right)^2\right)^{1/2}\right]^2\right\}^{-1/2} \tag{7}$$

Here, we recall that $n = 0, 1, 2, \ldots$ and $l \neq -1$. This is the Sommerfeld-Dirac fine-structure formula.

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Virtual Orbitals in Hartree-Fock Theory*

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An arbitrariness of virtual orbitals in the Hartree-Fock theory is discussed, and it is explicitly demonstrated that the energy spectrum of the virtual orbitals can be manipulated so that the convergence property may be improved in the perturbation theory and the configuration interaction calculation based on the Hartree-Fock equation.

INTRODUCTION

In the Hartree-Fock theory of many-electron systems, the occupied orbitals are the only orbitals physically relevant; but since we usually obtain the occupied orbitals from some kind of eigenvalue equations which give us more orbitals than needed to accommodate the electrons of the system, we have the so-called virtual orbitals. In many cases, they have no use and accordingly they are simply ignored.

There are certain cases, however, in which we do need to use those virtual orbitals resulting from the Hartree-Fock eigenvalue equation. Among them are the configuration interaction calculation and the perturbation calculation based on the Hartree-Fock solutions. As an example we shall discuss Kelly's many-body perturbation theory applied to Be.[1, 2]

For a closed-shell electron configuration of atoms and molecules, the Hartree-Fock operator F may be written (in a.u.)

$$F = -\tfrac{1}{2}\Delta - \sum_a (Z_a/r_a) + \sum_{i,\mathrm{occ}} (2J_i - K_i) \; , \tag{1}$$

and the Hartree-Fock equation is

$$F\phi_i = \epsilon_i\phi_i \; . \tag{2}$$

Here the suffix i numbers doubly occupied orbitals. The operators J_i and K_i are defined as follows:

$$J_i(\nu)\phi(\nu) = \int \phi_i^*(\mu)\phi_i(\mu)\frac{1}{r_{\mu\nu}}\, dV_\mu \times \phi(\nu) \; , \tag{3}$$

$$K_i(\nu)\phi(\nu) = \int \phi_i^*(\mu)\phi(\mu)\frac{1}{r_{\mu\nu}}\, dV_\mu \times \phi_i(\nu) \; . \tag{4}$$

For the $(1s)^2(2s)^2\,{}^1S$ state of the Be atom, we have

$$F = -\tfrac{1}{2}\Delta - (Z/r) + (2J_{1s} - K_{1s}) + (2J_{2s} - K_{2s}) \quad , \tag{5}$$

and $$F\phi_{1s} = \epsilon_{1s}\phi_{1s} \quad , \tag{6}$$

$$F\phi_{2s} = \epsilon_{2s}\phi_{2s} \quad . \tag{7}$$

Kelly first adopted the same operator to produce necessary virtual orbitals;

$$[-\tfrac{1}{2}\Delta - (Z/r) + (2J_{1s} - K_{1s}) + (2J_{2s} - K_{2s})]\phi_v = \epsilon_v\phi_v \quad . \tag{8}$$

This is Eq. (4.3) of his first paper,[1] and it turned out that all the virtual levels given by Eq. (8) were in the continuum.

If one uses the obvious relations,

$$(J_{1s} - K_{1s})\phi_{1s} = 0 \quad , \tag{9}$$

$$(J_{2s} - K_{2s})\phi_{2s} = 0 \quad , \tag{10}$$

Eqs. (6) and (7) are reduced to

$$[-\tfrac{1}{2}\Delta - (Z/r) + J_{1s} + (2J_{2s} - K_{2s})]\phi_{1s} = \epsilon_{1s}\phi_{1s} \quad , \tag{6$'$}$$

$$[-\tfrac{1}{2}\Delta - (Z/r) + (2J_{1s} - K_{1s}) + J_{2s}]\phi_{2s} = \epsilon_{2s}\phi_{2s} \quad . \tag{7$'$}$$

It is to be noted that, for the virtual orbitals, the Hartree-Fock operator as it is in Eq. (8) undergoes no such reduction.

In his second paper on Be, Kelly[2] turned to use the operator in Eq. (7′) to acquire the virtual orbitals needed in the perturbation calculation;

$$[-\tfrac{1}{2}\Delta - (Z/r) + (2J_{1s} - K_{1s}) + J_{2s}]\phi_v = \epsilon_v\phi_v \quad . \tag{11}$$

This is Eq. (13) of his second paper.[2] He made the choice in order to expedite the convergence of the perturbation expansion by generating discrete negative virtual energy levels. However, a drawback of the choice is that the new "(1*s*)" orbital differs from the Hartree-Fock (1*s*) orbital given by Eq. (6′), and all the *s*-type orbitals, except (2*s*), are not expected to be rigorously orthogonal to the original (1*s*) orbital, although it was shown that the orthogonalities hold to a high approximation.[2]

In the following, we shall first demonstrate explicitly an arbitrariness in our choosing the virtual orbitals which are orthogonal to the occupied orbitals in the Hartree-Fock theory and then we shall show, by utilizing the arbitrariness profitably, that the nonorthogonality problem mentioned above may be avoided while still retaining the desirable resemblance to the single-particle excitation of the system in the energy spectrum of the virtual orbitals. Finally, an illustrating numerical example will be given in the case of Hartree-Fock-Roothaan calculation of the He atom. The mathematical idea to be proposed in the following is a simplified version of the one discussed by Silverstone and Yin.[3]

ARBITRARINESS IN VIRTUAL ORBITALS

By the use of appropriate coupling operators,[4] one may bring the Hartree-Fock equation to the following form, including general open-shell cases:

$$R|\phi_i\rangle = |\phi_i\rangle\epsilon_i \quad . \tag{12}$$

The equation is primarily designed to yield the occupied orbitals of the system. The virtual orbitals should be regarded as a sort of by-product. Thus, the eigenvalues and the eigenfunctions of Eq. (12) can be divided into two rather distinct groups, the first group corresponding to the occupied orbitals and the second corresponding to the virtual orbitals.

Let us introduce the following operator V:

$$V = (1-P)\Omega(1-P) \quad , \tag{13}$$

where $$P = \sum_{i,\mathrm{occ}} |\phi_i\rangle\langle\phi_i| \tag{14}$$

is the projection operator which belongs to the so-called Hartree-Fock manifold and Ω is an arbitrary Hermitian operator. We shall now show that, by adding the operator V to the original operator R, physical characteristics of the second group can be changed without affecting the first. Let a new operator R' be

$$R' = R + V \quad ; \tag{15}$$

then it is easily established that for the occupied orbitals,

$$R'|\phi_i\rangle = R|\phi_i\rangle = |\phi_i\rangle\epsilon_i, \quad (i\text{: occupied}) \quad , \tag{16}$$

thus restoring the original form in Eq. (12), and for the virtual orbitals we have

$$R'|\phi_v\rangle = (R + \Omega - P\Omega)|\phi_v\rangle = |\phi_v\rangle\epsilon_v \quad . \tag{17}$$

CHOICE OF Ω

From Eq. (17), we have the equation

$$\epsilon_v = \langle\phi_v|R + \Omega|\phi_v\rangle \quad , \tag{18}$$

which suggests immediately one possible choice of the operator Ω in order to modify the energy spectrum of the virtual orbitals; an additional static potential energy operator

$$\Omega = U(r) \quad .$$

For the atomic case, we have

$$U(r) = (\alpha/r) \tag{19}$$

which can be a simple but yet interesting possibility, supplying an ion-core potential for the outermost "excited" electron.

More sophisticated choices of Ω can also be made. Let us take the beryllium case again as an example. In this case,

$$R=-\tfrac{1}{2}\Delta-(Z/r)+(2J_{1s}-K_{1s})+(2J_{2s}-K_{2s}) \quad , \tag{20}$$

and we choose Ω to be

$$\Omega=-(J_{2s}-K_{2s}) \quad . \tag{21}$$

Then we see immediately that

$$(R+V)\,|\,\phi_{1s}\rangle=R\,|\,\phi_{1s}\rangle \quad , \tag{22}$$

$$(R+V)\,|\,\phi_{2s}\rangle=R\,|\,\phi_{2s}\rangle \quad , \tag{23}$$

$$(R+V)\,|\,\phi_v\rangle=(R+\Omega-|\,\phi_{1s}\rangle\langle\,\phi_{1s}|\,\Omega)\,|\,\phi_v\rangle \quad . \tag{24}$$

From the above we conclude that for the (1*s*) and (2*s*) orbitals it amounts to use the same equations given in Eqs. (6′) and (7′) and for the virtual orbitals we use

$$[-\tfrac{1}{2}\Delta-(Z/r)+(2J_{1s}-K_{1s})+J_{2s}]\phi_v + \langle\,\phi_{1s}|\,(J_{2s}-K_{2s})\,|\,\phi_v\,\rangle\,\phi_{1s}=\epsilon_v\phi_v \quad . \tag{25}$$

The second term in the left-hand side makes Eq. (25) different from Eq. (11) which was used by Kelly in his second paper.[2] It is interesting to note that the eigenvalue spectrum should remain the same since

$$\epsilon_v=\langle\,\phi_v|[-\tfrac{1}{2}\Delta-(Z/r)+(2J_{1s}-K_{1s})+J_{2s}]\,|\,\phi_v\rangle \,, \tag{26}$$

and still all the virtual orbitals should be orthogonal to the original (1*s*) and (2*s*) Hartree-Fock orbitals since all of them are generated by a common operator $(R+V)$.

NUMERICAL EXAMPLE

As an illustration we shall treat the He atom in the Hartree-Fock-Roothaan approximation. We use five Slater-type functions of the form

$$\chi=[(2n)!]^{-1/2}(2\zeta)^{n+1/2}r^{n-1}e^{-\zeta r}Y_{00} \tag{27}$$

as the basis set for the Roothaan expansion and the choice of the parameters is given in Table I. The first two ζ's are taken from the best double-ζ calculation, and the choice of the rest of n's and ζ's is dictated by an intention of producing reasonable virtual orbitals corresponding to (1*s*)(2*s*), (1*s*)(3*s*), (1*s*)(4*s*),... excitations.

TABLE I. Basis set parameters.

	(nl)	ζ
χ_1	(1*s*)	2.915 569
χ_2	(1*s*)	1.454 603
χ_3	(2*s*)	$\frac{1}{2}$
χ_4	(3*s*)	$\frac{1}{3}$
χ_5	(4*s*)	$\frac{1}{4}$

TABLE II. Occupied and virtual orbitals.

α	−1.0	−0.5	0.0	0.5
ϵ_1			−0.918 129	
C_{11}			0.179 897	
C_{12}			0.844 129	
C_{13}			0.001 671	
C_{14}			−0.000 740	
C_{15}			0.000 253	
ϵ_2	−0.368 418	−0.074 780	0.004 060	0.032 282
C_{21}	−0.741 786	−0.124 977	0.001 813	−0.010 526
C_{22}	0.374 665	−0.159 136	−0.026 857	0.027 639
C_{23}	1.177 639	1.011 753	0.086 539	−0.122 435
C_{24}	−0.802 269	0.001 792	−0.033 746	0.511 743
C_{25}	0.358 601	0.032 809	1.002 234	−1.316 563
ϵ_3	−0.084 968	−0.023 319	0.023 269	0.079 891
C_{31}	0.140 081	−0.045 305	−0.018 633	−0.024 736
C_{32}	−0.070 054	−0.071 400	−0.017 005	0.041 092
C_{33}	−0.414 990	0.476 795	−0.077 585	−0.299 647
C_{34}	1.563 820	−0.350 487	1.582 519	1.742 077
C_{35}	−0.461 025	−0.802 850	−1.197 736	−0.963 614
ϵ_4	−0.041 389	0.001 196	0.140 992	0.293 541
C_{41}	0.064 854	0.066 557	−0.053 063	−0.137 528
C_{42}	−0.028 931	0.171 426	0.435 187	0.518 402
C_{43}	−0.245 607	−1.156 229	−1.677 518	−1.677 873
C_{44}	1.141 571	2.261 807	1.708 966	1.483 108
C_{45}	−1.587 007	−1.554 814	−0.816 839	−0.678 525
ϵ_5	0.686 395	1.912 464	3.271 182	4.657 730
C_{51}	−1.832 508	−1.977 387	1.982 169	1.978 010
C_{52}	1.934 623	1.956 803	−1.923 145	−1.902 023
C_{53}	−1.283 606	−0.824 120	0.662 903	0.589 050
C_{54}	1.164 562	0.714 102	−0.567 878	−0.502 230
C_{55}	−0.564 993	−0.340 377	0.269 587	0.238 035

First we perform an ordinary Hartree-Fock-Roothaan calculation on the ground state of the He atom with these five basis functions. The general form of the atomic orbitals is given by

$$\Psi_i=\sum_{p=1}^{5}C_{ip}\chi_p \quad . \tag{28}$$

The results can be seen in the third column of Table II. The total energy, −2.861 675 a.u., is close enough to the Hartree-Fock value of −2.861 680 a.u.

As for the choice of the operator Ω, let us try the simple idea indicated in Eq. (19). With $\alpha=-1.0$, for instance, the "virtual" electron will be seeing something akin to a He$^+$ ion at the center. The results for several values of α are shown in Table II. Mathematically, the implication is almost trivial. It simply means that there is an infinite amount of arbitrariness in the choice of virtual orbitals, the only restriction upon which is that they should be orthogonal to the original occupied orbitals.

From a practical point of view, however, the arbitrariness of the virtual orbitals may be utilized profitably in such a way that the convergence may be improved in the perturbation theory and the configuration interaction calculation based on the Hartree-Fock equation. It is hoped that the discussion presented here will also have some pedagogical value in furthering a sound understanding of the nature of virtual orbitals.

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Induced Anisotropy and Light Scattering in Liquids*

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A weak depolarized Rayleigh wing has been observed for liquid xenon and for several liquids composed of spherical-top molecules. The intensity contours for these liquids decrease exponentially with increasing frequency shift. This behavior is similar to that predicted for spectra of collision-induced scattering from gases.

The existence of a continuous depolarized spectrum of scattered light centered at the exciting frequency has long been known[1] for liquids composed of anisotropic molecules. This spectrum, commonly called the "Rayleigh wing," is believed to arise from orientation fluctuations of individual molecules and has been the subject of many papers.[1, 2] Depolarized scattering by liquids composed of spherical-top (tetrahedral) molecules has also been observed,[3] but is not well understood. Recently, Levine and Birnbaum[4] have discussed the scattering of light arising from the change in anisotropic polarizability produced in pairs of atoms or molecules during collision and have derived expressions for the intensity of the spectrum and the degree of depolarization. McTague and Birnbaum[5] have observed depolarized spectra of gaseous Ar and Kr at high pressure in general agreement with this theory, and they attribute the spectra to colliding pairs. Also, Thibeau and Oksengorn[6] have developed a theory based on the fluctuations of the internal field at each atom, which explains their observations on the depolarization of Rayleigh scattering in compressed Ar. We have observed depolarized spectra from liquid Xe, CCl_4, $SiCl_4$, $TiCl_4$, $SnCl_4$, $SnBr_4$, $C(CH_3)_4$, and $Si(CH_3)_4$. These spectra are all of very-low intensity; they have depolarization ratios of $\frac{3}{4}$ (for plane-polarized incident light); and they exhibit an exponential decrease in intensity with increasing frequency shift.

A He-Ne laser provided plane-polarized radiation of 50 mW power at 6328 Å. Reagent-grade liquids were filtered or vacuum distilled into glass Raman cells designed to minimize stray light. The cells were enclosed in a temperature-controlled metal block (±0.5°), and the liquids maintained at a temperature of 295°K, with the exception of $SnBr_4$ which was kept at 313°K. Research-grade Xe was liquefied and maintained at 164°K. Depolarized radiation scattered at an angle of 90° was selected by a polarizer placed between the sample and spectrometer. The scattered light was analyzed with a Spex 1400 double monochromator, the total instrumental width (laser plus spectrometer) being $1.7\ \mathrm{cm}^{-1}$ for a slit width of $100\ \mu\mathrm{m}$. A cooled photomultiplier tube (ITT-FW130) with a dark count of 2 to 3 per sec was used for detection. This was followed by photon-counting equipment and a chart recorder. The spectrometer-detector combination was calibrated for sensitivity to light of different polarization directions over the wavelength region 6000 – 7000 Å.

Depolarized spectra having a continuous distribution of intensity out to $50-100\ \mathrm{cm}^{-1}$, with a maximum at the exciting frequency were observed for all the liquids studied. The spectra are all of very-low intensity. For example, for Xe, the total integrated intensity is $\sim 10^{-3}$ of that of the polarized Rayleigh-Brillouin triplet; moreover, this spectrum disappears in solid Xe. The relative intensi-