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Calculation of excitation energies of atomic systems using the operator $\hat{O}\hat{A}\hat{O}^{\dagger}$

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An excitation Hamiltonian is formulated by adding an operator $\hat{O}\hat{A}\hat{O}$ to the Fock operation whose eigenvalue differences represent excitations of electronic systems. $\hat{O}$ is an operator which projects onto the virtual space of the Fock operator and $\hat{A}$ is chosen so that one has a Koopmans theorem and a variational principle for these states. The formalism is then used to calculate excitation energies of atomic He, Li, Be, and Na.

I. INTRODUCTION

One is very interested in finding an excitation operator whose eigenvalue differences will approximate the excitations of the atomic, molecular, or solid system under investigation to a high degree of accuracy (i.e., within experimental accuracy). The starting point in the past has centered around the Hartree-Fock equations where it has been shown by Koopmans's theorem that the eigenvalues of the Fock operator for the occupied orbitals represent ionization energies of the system (the $N-1$ system) if relaxation is neglected. However, when one looks at the virtual orbitals (unoccupied states), the Fock operator gives eigenvalues which are related to electron affinities, namely the $N+1$ system instead of the $N-1$ system.[1] This difficulty is inherent in all solutions of approximations to Dyson's equation[2] (of which the Hartree-Fock equation is the first-order approximation). In some systems where the excited state has the redistribution of charge distributed over a large volume (such as a Bloch-type charge going to another Bloch-type charge), the energy differences of solutions of Dyson's equation of the $N+1$ and $N-1$ systems match excitations of the N system. This situation is seldom realized in atomic and molecular systems and is not found in a large number of excitations in crystalline systems. Thus there exists a need to develop methods of obtaining excitations of the N system. In doing this, one is looking for a simple way to include the effect found in many excitations—that is, the excited state appears to have a localized hole and/or electron—without performing a configuration-interaction calculation.

To date, the excitation Hamiltonian used most in solid-state physics calculations has been the approximate Fock operator where the average free-electron-gas operator to the exchange term has been inserted. That is, a local approximation to the exchange term has been used instead of an operator which is a function of two electron coordinates. There is some arbitrariness to this operator, namely, whether one makes the approximation in the total energy equation (this leads to the Kohn-Sham approximation[3]) or whether one makes the approximation in the Fock operator after the variation of the total energy has been taken (Slater's approximation[4]). The ratio of the coefficients of the Kohn-Sham approximation to that of the Slater approximation is $\frac{2}{3}$ to 1. This has led to finding other ways of determining the coefficient, which most of the time falls between the above two values. In a lot of examples one simply introduces a parameter and adjusts the value to match a particular experimental value. In most cases this approximation does not match the Hartree-Fock eigenvalues which it is supposed to do nor does it match experiment. It causes the exchange energy to be underestimated and the ionization energies to be too small. In turn it also causes the $N+1$ eigenvalues to be too small. This sometimes matches experimental values of excitations to the N system; however, this is accidental. Thus one has to consider this approach as a parameter theory possibly without predictive capability.

In Ref. 1, Löwdin showed that if ρ is the first-order density matrix of the ground state and ρ' that for the single "excited" state (where $\rho' = \rho + \Delta\rho$), one has

$$\Delta\rho(1, 2) = \psi_a^*(1)\psi_a(2) - \psi_i^*(1)\psi_i(2) \ , \tag{1.1}$$

where ψ_a is an "excited" natural spin orbital and ψ_i is the "removed" natural spin orbital. Equation (1.1) was obtained using a Koopmans-like approximation. Such a ρ' charge density leads to a V^{N-1}

potential for the excited states.

Hunt and Goddard[5] also took special care in formulating the correct V^{N-1} potentials for excited states from closed-shell ground states. They maintained the correct spin state when they deleted the self-energy terms, namely singlet and triplet excited states. In the calculation of the occupied orbitals, these self-energy terms cancel automatically. This concept of generating improved virtual states from V^{N-1} potentials has been used extensively by Kelly[6] in calculating correlation energies in many-body perturbation theory. His V^{N-1} potential consisted of the $N-1$ occupied states where the ith state normally occupied is left unoccupied.

Expanding the above concepts one of the authors,[7] using a suggestion of Gilbert,[8] introduced an operator to be added to the Fock operator which would cause the virtual states to "see" a V^{N-1} potential, that is, an operator of the form $\hat{O}\hat{A}\hat{O}$, where $\hat{O}$ is a projectile onto the space of the virtual Fock orbitals and $\hat{A}$ is an operator which causes the virtuals to see the V^{N-1}-like potential. Scofield *et al.*,[9] using similar ideas, calculated the pair-correlation energies of oxygen, fluorine, and neon with virtual orbitals generated with an $\hat{A}=-\beta/r$.

It is the purpose of this investigation to describe the choice of $\hat{A}$ and present calculated results of one such $\hat{A}$. A discussion of the effects of relaxation and screening of the interaction is included. In Sec. II an outline of the excitation Hamiltonian is given. The results and comparison with other calculations and experiments are given in Sec. III. The conclusions are then given in Sec. IV.

II. $\hat{O}\hat{A}\hat{O}$ BACKGROUND

In obtaining an excitation Hamiltonian the first step considered here is to make sure that the excited states or virtual states see the correct type of field. Since in atoms and molecules plus a large number of crystals the excitations are localized, one wants to have this effect included in the excitation Hamiltonian. A localizing operator for the occupied space orbitals which will give the same charge density as the Hartree-Fock charge density has been suggested by Adams[10] and Gilbert.[8] Namely, one has

$$A=\hat{\rho}\hat{A}\hat{\rho} \, , \tag{2.1}$$

where $\hat{\rho}$ is the charge density operator of the Hartree-Fock operator and has the property

$$\hat{\rho}^2=\hat{\rho}=\hat{P} \, . \tag{2.2}$$

$\hat{A}$ is an arbitrary operator which is chosen to help reduce the computational problem. If ψ_i is a virtual orbital, one has

$$A\psi_i=\hat{\rho}\hat{A}\hat{\rho}\psi_i=0 \, . \tag{2.3}$$

On the other hand, if ψ_i is an occupied orbital, one has

$$A\psi_i\neq 0 \, . \tag{2.4}$$

Clearly the use of $\hat{\rho}$ as a projection onto the occupied space can be extended to form a projection operator onto the virtual space. One has simply

$$1=\hat{\rho}+(1-\hat{\rho})=\hat{P}+\hat{O} \, , \tag{2.5}$$

and one can form an operator B of the form

$$B=\hat{O}\hat{A}\hat{O} \, . \tag{2.6}$$

Here again $\hat{A}$ is an operator which is at present an arbitrary operator. In obtaining the correlation energy in Ref. 7, a substantial improvement of the rate of convergence of the configuration-interaction calculation was obtained over the use of normal solutions to the Fock equation. In this calculation $\hat{A}$ was a three-dimensional square well. The best results were obtained with a radius of the square well at 3 a.u. and a depth of 1 Ry. A similar basis set was generated in Ref. 9, and used in the linked-cluster many-body perturbation theory of Brueckner's[11] and Goldstone's[12] calculations. In this calculation the operator $\hat{A}$ was chosen to have the form $-\beta/r$ with $\beta=1$.

Let us now turn to the main objective of this note, that is, to formulate an $\hat{A}$ such that when $\hat{O}\hat{A}\hat{O}$ is added to the Fock operator, an operator is formed whose eigenvalues are the excitations of the system being investigated. The removal of an electron of a core state of an atom will leave behind a Coulomb potential of the form

$$V(\vec{r}_1)=\int \psi_c^*(\vec{r}_2)\frac{e^2}{|\vec{r}_1-\vec{r}_2|}\psi_c(\vec{r}_2)\,d\vec{r}_2 \, . \tag{2.7}$$

There will be some change in the charge density. Since we are looking at core states, the nuclear attraction is the major force, and the removed orbital or hole will retain nearly the same shape. However, the outer shells may relax substantially. (One has also an exchange potential which will be discussed later in this section.) The major change in the remaining electron charge density will come from the outer electron orbits. This gives the relaxation and causes the energy change between the ionized atom and the ground state to be less than the Hartree-Fock eigenvalue. This can be taken into account by obtaining self-consistent solutions of both the atom and ion and taking the total energy difference; or one could calculate to a high degree of accuracy the energy change caused by the mixing of the top orbitals through second-order perturbation theory, where the perturbation is the potential given in Eq. (2.7).

There is one more major effect which will be discussed more fully in Sec. III and taken into account in later calculations. That is, the excited electron will not see the exact potential of Eq. (2.7); rather, this potential will be screened by the outer electrons and thus somewhat reduced.

It is useful at this point to develop specific mathematical formulation of the ideas presented previously. We begin by defining a system Hamiltonian for an N-particle system in terms of general one-body operators f_i and two-body operators g_{ij}. We find

$$H=\sum_{i=1}^{N} f_i+\frac{1}{2}\sum_{\substack{i,j=1\\ i\neq j}}^{N} g_{ij} \ . \tag{2.8}$$

In terms of a Slater determinantal-type wave function, the form is

$$\begin{aligned}\Psi(x_1,\ldots,x_n)&=(N!)^{-1/2}\det[\psi_i(x_j)]\\ &=(N!)^{1/2}\hat{A}s\prod_{i=1}^{N}\psi_i(x_i) \ . \end{aligned}\tag{2.9}$$

Here $\hat{A}s$ is the antisymmetrizing operator and the ψ_i are spin orbitals. The energy E is given as

$$\begin{aligned}E&=\langle\Psi|H|\Psi\rangle\\ &=\sum_{i=1}^{N}\langle i|f_1|i\rangle+\sum_{i,j=1}\tfrac{1}{2}(\langle ij|g_{12}|ij\rangle-\langle ij|g_{12}|ji\rangle) \ .\end{aligned}\tag{2.10}$$

If the orbitals are not permitted to relax, the energy needed to remove an electron in state ψ_N is given as

$$\Delta E_N=\langle N|f_1|N\rangle+\sum_{i=1}^{N}(\langle iN|g_{12}|iN\rangle-\langle iN|g_{12}|Ni\rangle) \ . \tag{2.11}$$

Let us assume Ψ is the system ground state and the orbitals ψ are chosen so that the system energy is stationary; one finds that the orbitals ψ satisfy the Hartree-Fock equation

$$\begin{aligned}&\left(f_1+\int d\tau_2\sum_{i=1}^{N}|\psi_i(2)|^2 g_{12}\right)\psi_j(1)\\ &\qquad-\sum_{i=1}^{N}\psi_i(1)\int d\tau_2\,\psi_i^*(2)\psi_j(2)=\epsilon_j\psi_j(1) \ .\end{aligned}\tag{2.12}$$

The solutions to (2.12) fall into two classes. One class is for $i\leqslant N$, where one finds that ΔE_i as given by (2.11) is exactly equal to ϵ_i given by (2.12). This is a statement of Koopmans's theorem. However, there are solutions to (2.12) for which $i>N$. For such solutions Koopmans's theorem is not satisfied, and the eigenvalues are not ionization energies of the N-particle system. These orbitals are termed virtual and are labeled by a, b, etc., from here on. It is noted that the variable x includes space and spin degrees of freedom and that integration implies summation on spin variables.

Consider a ψ_a solution to (2.12) and also the energy needed to remove the electron in ψ_a from an N-body system, where ψ_a replaces ψ_N [as in (2.9)] and the ψ_i, where we adopt the convention that i, j are always less than or equal to N, are orbitals occupied in the ground state and are solutions to (2.12). We find

$$\Delta E_a=\langle a|f_1|a\rangle+\sum_{i=1}^{N-1}(\langle ai|g_{12}|ai\rangle-\langle ai|g_{12}|ia\rangle) \ . \tag{2.13}$$

However, the ϵ_a for (2.12) is given by

$$\epsilon_a=\langle a|f_1|a\rangle+\sum_{i=1}^{N}(\langle ai|g_{12}|ai\rangle-\langle ai|g_{12}|ia\rangle) \ , \tag{2.14}$$

demonstrating the previously discussed failure of Koopmans's theorem for the virtual orbitals.

Consider now an operator of form $\hat{O}\hat{A}\hat{O}$, where $\hat{A}$ is chosen to be

$$\hat{O}\hat{A}\hat{O}=\hat{O}[(-1)\langle N|g_{12}-g_{12}\hat{P}_{12}|N\rangle]\hat{O} \ . \tag{2.15}$$

$\hat{P}_{12}$ is defined such that

$$\langle a|\hat{O}\langle N|g_{12}\hat{P}_{12}|N\rangle\hat{O}|a\rangle=\langle aN|g_{12}|Na\rangle \ . \tag{2.16}$$

One may add $\hat{O}\hat{A}\hat{O}$ to (2.12) without disturbing the ground-state solution, so that the stationary condition is satisfied. The new equation for the orbitals is of the form

$$(F+\hat{O}\hat{A}\hat{O})\psi_i=\epsilon_i\psi_i \ . \tag{2.17}$$

For this equation we find for an ϵ_a using (2.15) that

$$\epsilon_a=\langle a|f_1|a\rangle+\sum_{i=1}^{N-1}(\langle ai|g_{12}|ai\rangle-\langle ai|g_{12}|ia\rangle) \ . \tag{2.18}$$

Thus for (2.17) and (2.15) one has a Koopmans's theorem for the virtual orbitals.

It is simple, furthermore, to show that in the unrelaxed orbital limit (Koopmans's limit) the difference in the eigenvalues of (2.17) using (2.15) are excitations of the N-particle system for single electrons. Assume the electron in the state N is excited to a state a. Call this energy for excitation ΔE_N^a. Using (2.10), if E_g is the total ground-state energy and E_N^a is the excited-state energy one has

$$E_n^a - E_g = \Delta E_N^a \equiv \langle a|f_1|a\rangle + \sum_{i=1}^{N-1} (\langle ai|g_{12}|ai\rangle - \langle ai|g_{12}|ia\rangle) - \langle N|f_1|N\rangle - \sum_{i=1}^{N-1} (\langle Ni|g_{12}|Ni\rangle - \langle Ni|g_{12}|iN\rangle) \equiv \epsilon_a - \epsilon_N\,. \tag{2.19}$$

Therefore the eigenvalue differences correspond to the excitation energies of the N-particle system for excitation from state $|N\rangle$. Please note that the choice of excitation orbital $|N\rangle$ is not special since any of the occupied states can be chosen to be $|N\rangle$.

This choice of $\hat{A}$ will lead to the same results as found in Ref. 5 for the triplet (the lowest excited state by Hund's rule); however, it will not reproduce the singlet case. For the triplet the exchange-like term is zero and $\hat{A}$ is just the Coulomb term (sometimes denoted as $-J_u$). To obtain the spin singlet, the choice of $\hat{A}$ would be $-J_u$ plus twice the exchange term (sometimes denoted as K_u). Using (2.15) as $\hat{A}$ and with the spin of the substituted orbit the same as that of the removed orbit, one has $\hat{A}$ equal to $-J_u + K_u$. Two points should be made. First, in complicated systems, for which this development of the excitation operator is intended, S^2 is not a good quantum number. Second, one needs, in general, more than one determinant for a trial wave function, even in simple systems, to obtain the correct spin symmetry. Thus in this work the pure spin-state requirement will be dropped. For the simple systems, such as the $1s2s$ excited state of He, an error of ~0.4 eV is found, and in Be, for the $1s^2 2s3s$ excited state, one obtains an error of ~0.3 eV.

Finally we consider the proper variational determination of the virtual ψ_a. We show that these are properly the solutions of (2.17) using (2.15) under the restriction of having only one Slater determinant. Consider a given set of orbitals ξ_i, $i \leqslant N-1$, for the self-consistent ground-state Fock equation. Choose the ξ_a so that the energy of the state

$$\Psi_N^a(x_1, \ldots, x_N) = (N!)^{1/2} \hat{A}_s \left(\xi_a(x_N) \prod_{i=1}^{N-1} \xi_i(x_i)\right) \tag{2.20}$$

is stationary with respect to $\xi_a \xi_a^*$. Requiring ξ_a to be orthogonal to the occupied orbitals leads to

$$\delta_{\xi_a^*}\left[E_N^a - \sum_{\substack{i=1,\\ i\neq a}}^{N-1} \lambda\left(\int \xi_a \xi_i^* \, d\tau - \delta_{ia}\right)\right] = 0\,, \tag{2.21}$$

with

$$E_N^a = \sum_{i=1}^{N-1} \langle i|f_1|i\rangle + \langle a|f_1|a\rangle + \frac{1}{2}\sum_{i=1}^{N-1}\sum_{j=1}^{N-1} (\langle ij|g_{12}|ij\rangle - \langle ij|g_{12}|ji\rangle) + \sum_{i=1}^{N-1} (\langle ai|g_{12}|ai\rangle - \langle ai|g_{12}|ia\rangle)\,. \tag{2.22}$$

The variation produces for the ξ_a the equation

$$\left(f_1 + \sum_{i=1}^{N-1} \int |\xi_i(2)|^2 g_{12}\, d\tau_2\right) \xi_a(1) - \sum_{i=1}^{N-1} \xi_i(1) \int \xi_1^*(2) \xi_a(2) g_{12}\, d\tau_2 = \lambda_a \xi_a(1)\,. \tag{2.23}$$

We see that the form for the expectation value of this operator with ξ_a is the same as for (2.17) using (2.15) for ψ_a. Thus if we show ψ_a to be the same as ξ_a, the ψ_a of (2.17) and (2.15) are those which minimize the system energy for unrelaxed ψ_i, $1 \leqslant N-1$.

The proof is to consider the matrix of the operator $\hat{B}$ defined by (2.23) with respect to the solution ψ_a of (2.17) and (2.15). We need to evaluate $\langle \psi_a|B|\psi_b\rangle$ in general. Now we know the operator in (2.17) is given as

$$F = \hat{B} + \int |\psi_N(2)|^2 g_{12}\, d\tau_2 - \phi_N(1) \int d\tau_2 \psi_N^\dagger(2) g_{12} \hat{P}_{12}\,. \tag{2.24}$$

Therefore

$$\begin{aligned}\langle \psi_a|\hat{B}|\psi_b\rangle &= \epsilon_a \delta_{ab} - \langle aN|g_{12}|bN\rangle + \langle aN|g_{12}|Nb\rangle \\ &\quad - \langle a|\hat{O}\hat{A}\hat{O}|b\rangle \\ &= \epsilon_a \delta_{ab} - \langle aN|g_{12}|bN\rangle + \langle aN|g_{12}|Nb\rangle \\ &\quad + \langle aN|g_{12}|bN\rangle - \langle aN|g_{12}|Nb\rangle \equiv \epsilon_a \delta_{ab}\,.\end{aligned} \tag{2.25}$$

Thus one finds that $\hat{B}$ is diagonal in the solution of (2.17) (2.15); hence the energy is minimized as desired.

We also note that for configuration-interaction calculations based upon single and double replacements of orbitals in the ground-state eigenfunction, the orbitals defined by (2.15) and (2.17) should be optimal to a good degree. For one thing, the virtual orbitals minimize the energy of the excited

TABLE I. Excitation triplet energies of the He atom. First column, experimental values taken from Ref. 13; Second column, calculated values using $\hat{O}\hat{A}\hat{O}$ where $\hat{A}$ is equal to V in Eq. (2.7); Third column, bound Hartree-Fock eigenvalue differences; Fourth column, values for the excitations by taking differences of total energies (Ref. 14). The ground and excited Hartree-Fock configurations in this case are both self-consistent.

Transition states	Expt (eV)	$\hat{O}\hat{A}\hat{O}$ Δ eigenvalues (eV)	Hartree-Fock Δ eigenvalues (eV)	ΔE_{tot} (eV)
$1s^2 \rightarrow 1s2s$	19.83	20.03	24.95	18.67
$1s^2 \rightarrow 1s3s$	23.00	23.36		21.54
$1s^2 \rightarrow 1s4s$	23.59	24.34		22.42
$1s^2 \rightarrow 1s5s$	23.97	24.71		•••
$1s^2 \rightarrow 1s2p$		21.30		19.84

wave functions, or, hence, minimize the energy differences between ground and excited wave functions. Thus in second-order perturbation theory the energy denominator is minimized. In addition, the interaction integral in the numerator is enhanced since the virtual orbitals see a V^{N-1} potential rather than a V^N potential and are much more spatially localized than the usual Fock virtual orbitals. The overlap of the virtual orbital with the occupied orbitals is thus enhanced using solutions of (2.15) and (2.17) in the same way as the work of Refs. 6, 7, and 9; hence, the interaction matrix elements are enhanced.

This theory may be considered a generalization and extension of the ideas introduced by Hunt and Goddard (Ref. 5) to solve the dilemma posed by having a V^N potential for the virtual orbitals. In the present theory, we have one operator for all excited states obtained by exciting from a specific ground-state orbital, whereas in the theory of Hunt and Goddard, excitation from a doubly occupied orbital leads to two Hamiltonians, one for the singlet and one for the triplet. In the present theory, the operator defining the occupied and unoccupied space is the same, whereas that of Hunt and Goddard is not. In addition, a series of desirable theorems have been proved in this section.

TABLE II. Excitation energies of the Li atom. First column, experimental values taken from Ref. 13; Second column, calculated values using $\hat{O}\hat{A}\hat{O}$ where $\hat{A}$ is equal to V in Eq. (2.7); Third column, bound Hartree-Fock eigenvalue differences. For the transition $1s^22s \rightarrow 1s^23s$ the energy is found to be 3.33 eV by taking the difference of total energies for the two configurations as obtained self-consistently (Refs. 15, 16).

Transition states	Expt (eV)	$\hat{O}\hat{A}\hat{O}$ Δ eigenvalues (eV)	Hartree-Fock Δ eigenvalues (eV)
$1s^22s \rightarrow 1s^23s$	3.37	2.85	5.11
$1s^22s \rightarrow 1s^24s$	4.34	4.15	5.18
$1s^22s \rightarrow 1s^25s$	4.75	4.72	
$1s^22s \rightarrow 1s^26s$	4.96	5.01	
$1s^22s \rightarrow 1s2s^2$	54.3[a]	62.14	67.25
$1s^22s \rightarrow 1s2s3s$		62.79	
$1s^22s \rightarrow 1s2s4s$		66.14	
$1s^22s \rightarrow 1s2s5s$		66.85	
$1s^22s \rightarrow 1s2s6s$		67.14	

[a] Value taken from J. A. Bearden and A. F. Burr, Rev. Mod. Phys. 39, 125 (1967).

III. RESULTS

The results of excited triplet atomic He are given in Table I. One finds very close agreement between experiment and the calculated values obtained using the $\hat{O}\hat{A}\hat{O}$ formalism described in Sec. II. As pointed out in Sec. II, $\hat{A}$ is defined by (2.7) as in all results presented in this section. The He atomic system should be the best for this choice of $\hat{A}$ because there is only one electron orbital which can screen and relax left in the system. Comparing the $\hat{O}\hat{A}\hat{O}$ results with Hartree-Fock, the first Hartree-Fock excited state is approximately 5 eV higher in energy than that of the experiment and $\hat{O}\hat{A}\hat{O}$. In fact, the mean deviation from experiment of the four $1s^2$ to $1sns$ excited states is ~0.5 eV. To get other types of excitation, such as $1s^2$ to $1snp$, one only needs to have a complete enough basis for the excited states. We added a few p-like basis functions and calculated the first p-like excited state, which is the bottom number in Table I.

Moving up the atomic table, the next example system investigated was atomic Li excited states, and the results are given in Table II. The first

TABLE III. Excitation triplet energies of the Be atom. First column, experimental values taken from Ref. 13; Second column, calculated values using $\hat{O}\hat{A}\hat{O}$ where $\hat{A}$ is equal to V in Eq. (2.7); Third column, bound Hartree-Fock eigenvalue differences.

Transition states	Expt (eV)	$\hat{O}\hat{A}\hat{O}$ Δ eigenvalues (eV)	Hartree-Fock Δ eigenvalues (eV)
$1s^22s^2 \rightarrow 1s^22s3s$	6.45	5.53	8.20
$1s^22s^2 \rightarrow 1s^22s4s$	7.99	7.11	8.32
$1s^22s^2 \rightarrow 1s^22s5s$	8.55	7.78	
$1s^22s^2 \rightarrow 1s^22s6s$	8.82	8.13	
$1s^22s^2 \rightarrow 1s2s^23s$	108.5[a]	124.15	128.48
$1s^22s^2 \rightarrow 1s2s^24s$		127.21	
$1s^22s^2 \rightarrow 1s2s^25s$		128.05	
$1s^22s^2 \rightarrow 1s2s^26s$		128.41	

[a] Value taken from Ref. a, Table II.

four rows give excitation of the outer electron from the $2s$ to $3s$–$6s$ states. The mean deviation of the first four rows is only ~0.2 eV. This means that the screening and relaxation effects are small or tend to cancel each other. In the fifth through ninth row the electron is removed from the inner orbit. One finds that relaxation about the hole in the lower orbit appears to be the major factor. The hole-electron interaction causes a change of about 5 eV, whereas the relaxation effects appear to be larger than 8 eV.

In the next example system, namely, triplet excitations of atomic Be, one sees a slightly different type of trend in the results of the first four rows of Table III. That is, the calculated $\hat{O}\hat{A}\hat{O}$ values underestimate the excitation from experiment with a mean deviation of 0.8 eV. Thus screening of the hole-electron interaction which is not included in the calculation is important and is mainly done by the remaining $2s$ electron. However, when the excitation is from the lower orbit, relaxation of the hole is again the major factor as can be seen in row five of Table III.

The excitation energies of atomic Na show the same general behavior as atomic Be in Table IV. This table includes different excitations, such as $3s$ to np and $2p$ to ns and np, for completeness. The first eight rows of Table IV shows the overbound effect of the calculation with a mean deviation of ~0.5 eV. It is surprising that although there are more electrons in Na than Be one finds less screening effects. The difference is that in

TABLE IV. Excitation energies of the Na atom. First column, experimental values taken from Ref. 13; Second column, calculated values using $\hat{O}\hat{A}\hat{O}$ where $\hat{A}$ is equal to V in Eq. (2.7); Third column, bound Hartree-Fock eigenvalue differences.

Transition states	Expt (eV)	$\hat{O}\hat{A}\hat{O}$ Δ eigenvalues (eV)	Hartree-Fock Δ eigenvalues (eV)
$1s^22s^22p^63s \rightarrow 1s^22s^22p^64s$	3.19	2.88	3.16
$1s^22s^22p^63s \rightarrow 1s^22s^22p^65s$	4.11	3.16	4.78
$1s^22s^22p^63s \rightarrow 1s^22s^22p^66s$	4.51	4.09	
$1s^22s^22p^63s \rightarrow 1s^22s^22p^67s$	4.71	4.41	
$1s^22s^22p^63s \rightarrow 1s^22s^22p^63p$	2.10	1.66	
$1s^22s^22p^63s \rightarrow 1s^22s^22p^64p$	3.75	3.29	
$1s^22s^22p^63s \rightarrow 1s^22s^22p^65p$	4.34	3.71	
$1s^22s^22p^63s \rightarrow 1s^22s^22p^66p$	4.62	3.74	
$1s^22s^22p^63s \rightarrow 1s^22s^22p^53s^2$		36.32	
$1s^22s^22p^63s \rightarrow 1s^22s^22p^53s4s$		37.89	
$1s^22s^22p^63s \rightarrow 1s^22s^22p^53s5s$		39.48	
$1s^22s^22p^63s \rightarrow 1s^22s^22p^53s6s$		40.28	
$1s^22s^22p^63s \rightarrow 1s^22s^22p^53s7s$		40.73	
$1s^22s^22p^63s \rightarrow 1s^22s^22p^53s3p$		36.26	39.73
$1s^22s^22p^63s \rightarrow 1s^22s^22p^53s4p$		39.62	
$1s^22s^22p^63s \rightarrow 1s^22s^22p^53s5p$		39.76	
$1s^22s^22p^63s \rightarrow 1s^22s^22p^53s6p$		40.06	
$1s^22s^22p^63s \rightarrow 1s^22s2p^63s^2$		71.22	
$1s^22s^22p^63s \rightarrow 1s^22s2p^63s4s$		72.77	
$1s^22s^22p^63s \rightarrow 1s^22s2p^63s5s$		74.37	
$1s^22s^22p^63s \rightarrow 1s^22s2p^63s6s$		75.17	
$1s^22s^22p^63s \rightarrow 1s^22s2p^63s7s$		75.62	
$1s^22s^22p^63s \rightarrow 1s^22s2p^63s3p$		71.16	
$1s^22s^22p^63s \rightarrow 1s^22s2p^63s4p$		74.51	
$1s^22s^22p^63s \rightarrow 1s^22s2p^63s5p$		74.51	
$1s^22s^22p^63s \rightarrow 1s^22s2p^63s6p$		74.95	
$1s^22s^22p^63s \rightarrow 1s2s^22p^63s^2$		1095.77	
$1s^22s^22p^63s \rightarrow 1s2s^22p^63s4s$		1096.24	
$1s^22s^22p^63s \rightarrow 1s2s^22p^63s5s$		1098.93	
$1s^22s^22p^63s \rightarrow 1s2s^22p^63s6s$		1099.55	
$1s^22s^22p^63s \rightarrow 1s2s^22p^63s7s$		1100.03	
$1s^22s^22p^63s \rightarrow 1s2s^22p^63s3p$	1071.1[a]	1094.36	
$1s^22s^22p^63s \rightarrow 1s2s^22p^63s4p$		1098.89	
$1s^22s^22p^63s \rightarrow 1s2s^22p^63s5p$		1099.07	
$1s^22s^22p^63s \rightarrow 1s2s^22p^63s6p$		1099.51	

[a] Value taken from Ref. a, Table II.

the case of Na one has a closed-shell core remaining whereas Be does not.

IV. CONCLUSIONS

It has been demonstrated that one can form an excitation Hamiltonian whose eigenvalue differences between occupied and virtual states represent excitation energy. By adding an operator to the Fock operator of the form $\hat{O}\hat{A}\hat{O}$ which only rotates the virtual space and by making a particular choice of $\hat{A}$, one has a variational principle and a Koopmans theorem for these states. With particular choices of $\hat{A}$, one can have local excitations which will turn out to be of great importance as the study is extended to molecules and solids. For the lower-energy states it was also found in this study that the relaxation of the hole state is important. This effect is also important when one studies solids, since the same type of behavior will be found in these systems. Overall, the obtaining of excitation energies from first principle of real systems has been overlooked for some time; so this study appears to be a major step in the right direction. There seems to be one conclusion related to solid-state physics to be drawn from this study. This is for the case of core excitations (soft x-ray spectroscopy): charge cloud relaxation effects may well be far more important than direct electron-hole interaction.

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