Moments of the dipole oscillator strength distribution and mean excitation energies of helium

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The $S(\mu)$ and $L(\mu)$ moments of the dipole oscillator strength distribution and the associated mean excitation energies I_μ have been calculated for the helium atom using the polarization-propagator formalism. It is found that, if correlation is included, agreement with experimental and other theoretical values is good. The mean excitation energy for stopping is found to be $I_0 = 42.41$ eV.

I. INTRODUCTION

The moments of the dipole oscillator strength distribution (DOSD) of a system are of considerable interest, as they are related to many physically interesting quantities. The μth moments of the DOSD are defined as

$$S(\mu) = \int E^\mu \frac{df}{dE} dE , \tag{1}$$

$$L(\mu) = \int E^\mu \ln E \frac{df}{dE} dE , \tag{2}$$

and

$$\ln I_\mu = \frac{L(\mu)}{S(\mu)} , \tag{3}$$

where E and f label the excitation energies and oscillator strengths of the system, respectively. The I's are referred to as the mean excitation energies of the system, and are related to quantities such as the stopping ($\mu = 0$) and straggling ($\mu = 1$) of swift, massive particles in matter, the Lamb shift ($\mu = 2$), electronic excitation ($\mu = -1$), and the static polarizability ($\mu = -2$).[1] Similarly, many of the L's and S's can be related to physically measurable quantities.

As the interest in these quantities is high, there has been considerable effort expended in their determination. As the full excitation spectrum (both excitation energies and oscillator strengths) of the system is necessary to determine the moments, it is difficult to calculate them directly. Thus emphasis has been placed on ascertaining them semiempirically. In particular, Meath and co-workers[2] have published a long series of papers reporting various properties of the DOSD's of various atoms and molecules.

There have been several first-principles calculations of the DOSD of atoms, most notable those of Inokuti and co-workers,[3-5] which are derived from Hartree-Fock-Slater (Herman-Skillman) wave functions. Although these calculations are rigorous and very extensive, encompassing all the atoms in the first four periods, they involve several severe approximations, and, being derived from Hartree-Fock-like wave functions, are uncorrelated. More recently, Rosendorff et al.[6] have introduced a method, based on that of Dalgarno and Lewis,[7] to calculate several of the I_μ moments which requires only initial-state wave functions as input. They report I_μ for H and He. For H the results are exact, but for He the calculations are based on Hartree-Fock, thus uncorrelated, wave functions.

In the past several years, we have developed a method for determining moments of the DOSD which is based on the polarization-propagator formalism,[8,9] and, like the method of Rosendorff et al., requires only initial-state data as input. Unlike their method, however, this method is not restricted to $-1 \le \mu \le 2$, and in principle all moments could be calculated. To compare the two methods, we report here our calculations on the DOSD of He.

II. METHODOLOGY

Direct calculation of the moments of the DOSD from Eqs. (1)–(3) requires integration over, and therefore knowledge of, the complete oscillator strength distribution of the system. We calculate these directly, without determining the eigenstates of the system and their energies, from the poles and residues of the polarization propagator, defined as[10]

$$\langle\langle r_a; r_b \rangle\rangle_E = \sum_{n(\neq 0)} \left[\frac{\langle 0|r_a|n \rangle\langle n|r_b|0 \rangle}{E - E_n + E_0} - \frac{\langle 0|r_b|n \rangle\langle n|r_a|0 \rangle}{E + E_n - E_0} \right] . \tag{4}$$

Here the sum is over all excitations out of the reference state 0 into state n, and r_a and r_b are components of the dipole operator $\mathbf{r}$. The dipole length oscillator strengths can then be calculated (in hartree atomic units) from

$$f_{0n} = \tfrac{2}{3} \langle 0|\mathbf{r}|n \rangle \cdot \langle n|\mathbf{r}|0 \rangle E_{0n} . \tag{5}$$

Similarly, the residues of the polarization propagator $\langle\langle p_a;p_b\rangle\rangle_E$ yield the oscillator strengths in the dipole velocity representation. The excitation energies are simply $E_{0n}=E_n-E_0$.

Solution of the equation of motion for the polarization propagator at various levels of sophistication leads to a hierarchy of approximations to the exact solutions. We consider here that the reference state is the ground state. In the normal implementation, the zeroth-order solution uses the Hartree-Fock (HF) ground state as the reference state, and single determinants composed of unrelaxed HF ground-state orbitals as representations of the excited states. The simplest extension of the zeroth-order approximation is to represent the excited states with a monoexcited configuration-interaction (MECI) wave function, which adds correlation to the excited, but not the ground state. The consistent first-order approximation to the propagator is the random-phase approximation (RPA) where correlation is introduced into both ground and excited states. Post RPA correlation corrections can also be introduced. The next level which is normally implemented is the consistent second-order polarization-propagator approximation (SOPPA),[11] and the third order is underway.[12] It should be noted that the HF, MECI, and RPA excitation energies and oscillator strengths can be obtained from a single diagonalization, while the SOPPA excitation energies are eigenvalues of an energy-dependent matrix.[11] Consequently, for consistent results one must iterate on each excitation energy separately. Since, for the basis we use, there are not too many allowed excitations, this is feasible.

In all propagator calculations finite basis sets are used, leading to a finite number of excitations corresponding to the number of particle-hole excitations allowed by the basis. Thus we approximate the continuum excitations by a finite number of discrete excitations into the continuum. For average properties such as the moments of the DOSD, this procedure works very well indeed,[8,13] but in such a case, no significance can be attached to individual states placed in the continuum.

The calculations reported here were done using the MUNICH program system.[14] We employed a basis set of 70 uncontracted Gaussian-type orbitals (GTO's), obtained using the $(13s11p6d)$ contracted to $[13s11p4d]$ basis of Jaszunski and Roos.[15] This basis admits a total of 33 allowed transitions, 11 with each of the Cartesian polarization directions.

As the Thomas-Reiche-Kuhn (TRK) sum rule

$$S^L(0)= \sum_{n(\neq0)} f^L_{0n}=N \ , \qquad (6)$$

$$S^V(0)= \sum_{n(\neq0)} f^V_{0n}=N \qquad (7)$$

should be obeyed exactly at the RPA level of approximation for a complete basis,[10] it can be used as a measure of the goodness of the basis. The agreement of the oscillator strength sums with the number of electrons indicates how complete the basis is, while the agreement between the length and velocity forms indicates how well the basis is balanced. At the RPA level, we find $S^L(0)=2.000\,025$ and $S^V(0)=1.999\,983$, indicating that the basis is both nearly complete and well balanced. The self-consistent-field (SCF) total energy for the basis is $E_{\mathrm{SCF}}=-2.861\,674\,34$ a.u., which can be compared to the Hartree-Fock limit value of Clementi and Roetti[16] of $E_{\mathrm{HF}}=-2.861\,6799$ a.u.

III. RESULTS AND DISCUSSION

The first few dipole allowed excitation energies and oscillator strengths of He as calculated at the SOPPA level are presented in Table I. For comparison we also show some SOPPA excitation energies obtained using a Slater-type orbital (STO) basis[17] and the experimental excitation energies and oscillator strengths.[18] The excitation energies and oscillator strengths for the first two transitions compare very well with the experimental values, but deteriorate for higher excitations. The third calculated excitation is already higher than the first ionization threshold [24.580 eV (Ref. 18)]. The reason that we do poorly for the higher excitations is that we do not have enough diffuse p orbitals in the basis to represent transitions of the type $1snp\leftarrow1s^2$ for $n\geq3$, as can be seen from the comparison with the other SOPPA calculation[17] which uses a more diffuse basis set.

In Table II we present the $S(\mu)$ [Eq. (1)] moments for $-6\leq\mu\leq1$ calculated at various levels of approximation. It is difficult to assess the quality of the results presented here by direct comparison, as there are few consistent sets of literature values available for most of the moments reported, and experimental values for only a few of the moments. The only firm touchstone is the TRK sum rule in RPA [$S(0)=2$] which is fulfilled in these calculations. [It should be noted that for a complete basis the TRK sum rule is exact for RPA, while it is only fulfilled through second order in SOPPA, leading to better $S(0)$ values in RPA than in SOPPA.] We include the results of Thakkar,[19] Cummings,[20] and Dehmer, Inokuti, and Saxon[3] (DIS), each of which is a consistently calculated set of moments, for comparison. (An extended tabulation

TABLE I. SOPPA excitation energies and oscillator strengths for the $1s\rightarrow(n+1)p$ excitations of He.

	This work		Jørgensen et al. (Ref. 17)	Experiment (Ref. 18)	
n	E_{0n} (eV)	f_{0n}	E_{0n} (eV)	E_{0n} (eV)	f_{0n}
1	21.327	0.269	21.28	21.217	0.276
2	23.152	0.080	23.04	23.085	0.073
3			23.66	23.741	0.030
4			23.98	24.045	0.015

TABLE II. $S(\mu)$ sum rules for He in the dipole length approximation (hartree atomic units).

	$S(-6)$	$S(-5)$	$S(-4)$	$S(-3)$	$S(-2)$	$S(-1)$	$S(0)$	$S(1)$
SOPPA	1.9841	1.7152	1.5245	1.4113	1.3919	1.5264	2.0391	4.2261
RPA	1.7294	1.5266	1.3864	1.3119	1.3222	1.4785	2.0000	4.0877
MECI							2.1727	
HF							2.3795	
Thakkar (Ref. 19)	2.0404	1.7499	1.5210	1.4150	1.3831	1.5049	1.9965	
DIS (Ref. 3)	3.231	2.591	2.131	1.818	1.645	1.644	1.999	3.854
Cummings (Ref. 20)				1.43	1.487	1.579	2[a]	3.81557
Accurate					1.3831[b]	1.5050[c]	2	4.0837[c]

[a]Constraint on the calculation.
[b]Experimental value, Ref. 23.
[c]Pekeris, Ref. 24.

of other calculated S and L moments for first row atoms is available in Ref. 3). The results of Thakkar[19] are computed via a perturbation variation scheme using an explicitly correlated wave function (constructed using the generator coordinate method) and should be normative. Our best (SOPPA) results agree well (~2%) with them. The advantage of the present method is that it can easily be extended to larger systems. The results of Cummings are calculated in the Hartree-Fock approximation, while the DIS results[21] comprise the set of moments obtained using the HF-like formalism with Herman-Skillman (local density functional) wave functions discussed earlier. Both methods utilize some constraints on the calculation which assure that the TRK sum rule is fulfilled. This is equivalent to renormalizing the calculations, and as such it is not straightforward to determine the effect of the renormalization on the other $S(\mu)$'s. The question of whether or not the DIS results contain correlation is problematical. The calculations use a HF formalism, which is, by definition, without correlation, but employ wave functions generated using a method which is sometimes claimed to include some degree of correlation.[22]

As the level of calculation increases from HF to MECI to RPA and finally to SOPPA, some correlation is first introduced in the excited states (MECI), then in the ground state to a lesser (RPA) or greater (SOPPA) extent. As correlation is not so important in He, none of the excitation energies changes much as correlation is included to a greater extent in the calculation. The oscillator strengths do change for the middle-lying excitations ($1snp \leftarrow 1s^2, n = 5,6,7$), however, giving up some 15% of their oscillator strength to the rest of the excitations. This leads to a gradual increase in $S(\mu < 0)$ and a de-

crease in $S(\mu > 0)$ as correlation increases. The changes are small, however, compared to cases where correlation is more important, such as Be.[9]

In hartree units, the static polarizability of the atom is equal to $S(-2)$. The exact value of $\alpha(0) = 1.383$ a.u. (Ref. 23) differs from our SOPPA value by only 0.5%, giving some measure of the reliability of the calculation. This result is much closer to the experimental value than earlier that of DIS or of Cummings, which is not too surprising considering that neither of those calculations is correlated. Similarly, the $S(-1)$ moment is in better agreement with the accurate calculation of Pekeris[24] even though the absolute agreement is not as good as for $S(-2)$. For the $S(1)$ moment we see the onset of the problem created by representing the high-lying continuum excitations with a finite basis set.

The situation is similar for the case of $L(\mu)$, presented in Table III, except that there are no experimental data to compare to. Some theoretical values are available, and we include in the table the values of DIS as well as some values obtained from moment theory.[25] It is clear that correlation makes little difference in the calculation of the $L(\mu)$ moments. In the case of $S(\mu)$ the variation of the moments came from variation of the oscillator strengths, the excitation energies varying only little. Here, one might consider that the oscillator strengths are multiplied by a smoothing function, $\ln E$, giving rise to an even smaller variation in $L(\mu)$ on inclusion of correlation. The results agree well with both moment theory[25] and DIS in the range $-1 \leq \mu \leq 1$, but we find DIS obtain moment values which are numerically too large for smaller values of μ.

Perhaps more interesting quantities than the moments

TABLE III. $L(\mu)$ sum rules for He in the dipole length approximation (hartree atomic units).

	$L(-6)$	$L(-5)$	$L(-4)$	$L(-3)$	$L(-2)$	$L(-1)$	$L(0)$	$L(1)$
SOPPA	−0.3106	−0.2288	−0.1529	−0.0712	0.0410	0.2582	0.9048	4.9205
RPA	−0.2351	−0.1712	−0.1088	−0.0373	0.0688	0.2754	0.9006	4.4358
MECI							1.0382	
HF							1.2478	
DIS (Ref. 3)	−0.745	−0.543	−0.383	−0.244	−0.099	0.121	0.711	4.163
Moment						0.248	0.870	4.53
Theory (Ref. 25)						±0.003	±0.015	±0.25

TABLE IV. I_μ (eV) for He.

	$I(-4)$	$I(-3)$	$I(-2)$	$I(-1)$	$I(0)$	$I(1)$
		This work (dipole length)				
SOPPA	24.62	25.87	28.02	32.23	42.41	87.18
RPA	25.16	26.45	28.66	32.78	42.69	80.54
		Shimamura and Inokuti				
Upper bound		(Ref. 26)		32.06	42.33	85.76
Lower bound				31.99	41.99	78.69
		DIS (Ref. 3)				
	22.74	23.80	25.62	29.29	38.84	80.14
		Rosendorff and Schlaile				
		[Ref. 6(b)]		31.01	39.96	76.64

of the DOSD themselves are the mean excitation energies I_μ, as they correspond more closely to measurable quantities. In Table IV we present our calculated values of I_μ. We also include the upper and lower bounds to the I_μ calculated by Shimamura and Inokuti[26] (SI), along with results of DIS, and some values calculated recently by Rosendorff and Schlaile[6(b)] (RS). Generally the agreement between our numbers and those of SI is very good, even though the moments used by SI to calculate their bounds come from a variety of sources. Agreement with DIS is reasonable, our correlated results generally being of the order of 10% larger than those of DIS. This is a somewhat smaller difference than we found in Be,[9] but the latter is a case where correlation is especially important. We also note in the case of He, as in other calculations,[8,9] that the bigger change in the I_μ comes on the initial addition of correlation to the calculation (i.e., from HF to RPA). Additional correlation beyond RPA tends to change the I_μ's only by a further small amount.

If we compare to the results of RS,[6(b)] we find that their results tend to be consistently higher than those of DIS for $\mu = -1, 0$ but lower for $\mu = 1$.

The quantity which is easiest to compare to experiment

TABLE V. Mean excitation energies of He.

	I_0 (eV)	Reference
	This work	
SOPPA	42.41	
RPA	42.69	
MECI	43.88	
HF	46.69	
	Other theoretical values	
Shimamura and Inokuti	42.161	26
Rosendorff and Schlaile	39.96	6(b)
Aashamar and Austvik	39.52	27
DIS	38.84	3
	Experimental values	
Janni	39.1	28
ICRU37	41.8	29
Ahlen	42.3	30
Andersen and Ziegler	41.7	31

is the mean excitation energy for stopping, I_0. In Table V we present our calculated values of I_0 at various levels of approximation, and compare them to other representative calculated and measured values. Helium should be nearly ideal for comparison of theoretically with experimentally determined I_μ's. The sample is a monoatomic gas, and should behave very much like a theoretical isolated atom. The gas is easy to handle, and no untoward experimental conditions are expected. The atomic number is low so that there will not be relativistic effects to consider. In spite of these considerations, it is not easy to extract a mean excitation energy from experiment,[32] and care must be taken in doing so. Comparison of our correlated results with those of Shimamura and Inokuti,[26] generally considered the best of the available theoretical results, and with the experimental results shows very good agreement. It is clear that the HF level calculations, DIS and RS, are too low by at least 2 eV.

IV. SUMMARY

The moments of the dipole oscillator strength distribution of He have been calculated in the polarization-propagator approximation up through second order in the fluctuation potential. As in previous cases,[8,9] the inclusion of correlation is very important in order to get reliable values of the $L(\mu)$ and $S(\mu)$ moments and of the mean excitation energies I_μ. Most of the improvement is already present in first order (RPA), although there are some changes when correlation is included to second order (SOPPA). Where it is possible to compare moments to experiment, agreement with our calculated numbers is good. The most reliable quantity to compare with is, perhaps, the mean excitation energy for stopping, I_0, which we calculate to be 42.41 eV. This is higher by some 1.5% than the recommended[29] experimental value.

The basis set used in this study is reasonably complete, as seen from the TRK sum rule. The greatest deficiency is apparently in the most diffuse orbitals, as seen by the deterioration of the excitation energies for the higher excitations. This is reflected in moments as well, and the large μ moments are not as reliable as those with smaller values of μ. This is simply a reflection of the higher powers of the excitation energy in those moments.

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$$S^H(\mu) = 2^{-\mu} S^R(\mu) \ ,$$

$$L^H(\mu) = 2^{-\mu}[L^R(\mu) - S^R(\mu)\ln 2] \ ,$$

$$I_\mu = R \ \exp[L^R(\mu)/S^R(\mu)] = 2R \ \exp[-L^H(\mu)/S^H(\mu)] \ .$$

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