

Full-potential scattered-wave calculations for molecules and clusters: Fundamental tests of the method

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We describe the testing of a non-muffin-tin extension to the scattered-wave method (due to Natoli, Benfatto, and Doniach [Phys. Rev. A **34**, 4682 (1986)]) for the calculation of one-electron energy eigenvalues and photoionization cross sections of molecules. For bound states the hydrogen molecular ion is used, and for continuum photoionization an ionized lithium pseudocluster is used, these being excellent tests because the analytic results are also known. Comparison of the results shows that the theory is correct and that the computational approach is feasible.

I. INTRODUCTION

We have recently developed computer programs to implement the full-potential scattered-wave (FP SW) theory of Natoli, Benfatto, and Doniach¹ for the calculation of bound and continuum electronic states in molecular clusters. In this version of the method the usual "muffin-tin" (MT) approximation to the electron-molecule potential is not made, so that the full one-electron potential may be used directly. Both the theory and the corresponding programs are quite complicated and it is necessary that some unequivocal way of testing them be found, before they are used for more interesting physical systems. The tests that we describe in this paper are for simple (but not trivial) systems which are free of extra physical complications and show clearly the benefits that accrue from the relaxation of the MT approximation.

The SW method has been used for many years with considerable success. In crystalline solids, where it is known as the Korringa, Kohn, and Rostoker (KKR) method,² it has been used to calculate band structures. A version of the method for the bound states of molecules and clusters was developed by Johnson and co-workers,³ and extended by others to continuum states⁴ with application to electron-molecule scattering and photoionization.⁵ In the molecular case it is normally used in a self-consistent-field (SCF) mode with Slater's $X\alpha$ approximation to exchange correlation, in which case it is called the SCF SW $X\alpha$ method. A relativistic version called the Dirac-scattered-wave (DSW) method has also been developed, which is based on a SW solution of the one-electron Dirac equation.⁶

In all these versions of the SW method the MT approximation is relied upon to provide mathematical tractability. In this approximation, introduced by Slater⁷ in the context of the augmented-plane-wave (APW) method, the atoms are enclosed by nonoverlapping spheres and the whole molecule enclosed in an outer sphere (OS) which intersects none of the atomic spheres. Within an atomic-

sphere region (ASR) the potential is spherically symmetrized about the nuclear position, while in the extramolecular region (EMR—that outside the OS) the potential is spherically symmetrized about the center of the OS. In the interstitial region (IR—that inside the OS, but outside all the ASR's) the potential is approximated by its average over that region.

The MT-based SW method has several attractive features. Firstly it is a non-basis-set, real-space method in which the wave functions are expanded in rapidly convergent partial-wave series around each atomic site. It is an *ab initio* technique and can accommodate a wide variety of molecular types at reasonable computational cost. For many years it has been realized that the major limiting factor of the MT SW method is the MT approximation itself, particularly in open, covalently bonded systems. *Ad hoc* schemes to improve the approximation, like overlapping atomic spheres⁸ or the inclusion of empty interstitial spheres,⁹ tend only to emphasize the sensitivity of the results to arbitrary (and unphysical) choices of parameters such as atomic-sphere radii. A variety of more sophisticated schemes has also been proposed over the years,¹⁰ trying to include higher multipoles of the potential in the ASR's and EMR or the true potential variation in the IR. In general, this is to be achieved at the cost of greatly increased complication. A promising approach is that of Williams and Morgan,¹¹ who generalized the ASR's to space-filling polyhedra, eliminating the IR altogether. In recent years their scheme has enjoyed a renewal of interest, especially in the work of Faulkner¹² and of Brown and Ciftan,¹³ although several other authors have also made important contributions.¹⁴⁻¹⁸ Unfortunately, a controversy exists among these authors about the mathematical formulation of the scheme, so that its status remains unclear. Our paper is intended to show that, at least with the formalism of Natoli, Benfatto, and Doniach, a valid, full-potential (i.e., non-MT) extension to the SW method is available and computationally feasible.

II. THEORY

The basis of the FP extension to the SW theory (for molecules) was given by Natoli, Benfatto, and Doniach¹ with some further developments (particularly for the bound-state case) given by Foulis.¹⁹ (We intend to submit for publication at a later date a full exposition of the FP SW theory and details of its numerical implementation.) The central part of the theory is the solution of the one-electron Schrödinger equation, approached (for both bound and continuum states) through its integral equation form. The same partition of space with spherical boundaries is made as in the MT case, but higher multipoles of the potential are retained in the ASR's and EMR, and the variation of potential in the IR is taken into account. Details of the construction of a sufficiently accurate representation of the potential are given elsewhere.²⁰ As usual one is led to a matrix secular equation,

$$\underline{S}\mathbf{B}=\mathbf{F} \quad (1)$$

whose solution vector \mathbf{B} determines coefficients in the expansions of the wave function. For continuum states the appropriate boundary conditions are imposed via the inhomogeneous part \mathbf{F} . For bound states \mathbf{F} is zero and so, to obtain a nonzero \mathbf{B} , the determinant of \underline{S} (a function of energy) must be zero. This only occurs for certain discrete values of the energy and so the eigenvalues are determined.

The most difficult computational task is the construction of the secular matrix \underline{S} and, in the FP version of the method, this difficulty is greatly compounded by the increase in complexity. In the FP SW theory, the secular matrix may be expressed as

$$\underline{S}=\underline{t}^{-1}+\underline{H}+\underline{T} \quad (2)$$

Here \underline{t} is a block-diagonal matrix whose individual blocks are, within a numerical factor, the usual atomic t matrices relative to the potentials in the ASR's (and the analogous one for the EMR). (Note that these matrices are, in principle, infinite dimensional and a truncation of the partial-wave expansions is required to make them finite.) In the MT case, because of the spherical symmetry of the ASR and EMR potentials, \underline{t} is diagonal; however, in the FP case the higher multipole components in these potentials cause coupling of the different radial equations in the partial-wave expansions, so that off-diagonal matrix elements appear in \underline{t} . The "structure factors" (or "propagators") \underline{H} depend only on the energy and the interatomic vectors, and are the same for the FP as for the MT case. The matrix \underline{T} appears only in the FP case and may be related to a t matrix for the IR potential. In our implementation of the FP SW theory we make the Born approximation for \underline{T} , taking advantage of the relative weakness of the IR potential (which we further diminish by resetting the zero of energy to the average of the potential over the IR).²¹ In this approximation the matrix elements of \underline{T} become two-center integrals over the IR, which involve only the energy, the interatomic vectors, and the IR potential.

III. NUMERICAL IMPLEMENTATION AND TESTING STRATEGY

Our numerical implementation of the FP SW theory consists in the development of two computer programs ENESHX (a mnemonic for "energy eigenvalue search for potentials represented as spherical harmonic expansions") and CNTSHX ("continuum photoionization cross sections for potentials"), and some associated programs which we do not discuss here. In broad outline they were written following the basic pattern of the analogous programs of Smith and Johnson³ and Natoli,⁵ using as much of their actual code as was still relevant for the FP case. As in these MT programs use is made of molecular point symmetry to reduce the size of the secular matrix.²² Great effort was made to develop programs of sufficient generality to accommodate a wide variety of molecules and to explore in some depth the nature and importance of non-MT corrections. These large programs (roughly 4000 FORTRAN lines each) can be run on even small computers (like the VAX and micro-VAX series) in reasonable times (a few hours) for molecules with a central atom and up to, say, three shells of (symmetry-equivalent) coordinating atoms.

The essence of the non-MT corrections is contained in the off-diagonal elements of \underline{t} and in \underline{T} . For each ASR block (and the EMR block) of \underline{t} the radial Schrödinger equations are coupled and we use the matrix Numerov method to solve them, using the asymptotic form of the matrix solution at zero radius (for the ASR's) or infinite radius (for the EMR) to start the integrations. From the matrix solutions and their derivatives at the sphere radii the individual blocks of \underline{t} are readily calculated. For \underline{T} the crucial innovation is a flexible and accurate way of calculating the IR integrals. The main difficulty here stems from the awkward topology of the IR and the fact that it varies from one molecule to another. Numerical quadratures of Gaussian quality are, in general, not available for such regions. Instead our quadrature mesh for a given molecule is a composite made from high-quality meshes for spherical volumes. Firstly we use a large one to integrate over the interior of the OS. Then small ones are used to subtract off the integrals in the ASR's. The spherical meshes that we use are products of normal Gauss-Legendre (or Gauss-Jacobi) radial meshes with spherical surface meshes from the book of Stroud.²³ For the OS we use a large and very accurate surface mesh due to Lebedev.²⁴ The flexibility that we obtain in this way is somewhat offset by another problem which then arises. Because the integrands have singularities at the atomic nuclei and would therefore upset the numerical quadrature, we replace them within the ASR's by well-behaved functions matched smoothly at the sphere boundaries with the true integrands in the IR.

Our general strategy for the development and testing of ENESHX and CNTSHX was as follows. First we wrote ENESHX and used it to search for the eigenvalues of the hydrogen molecular ion H_2^+ . The bound-state part of the FP SW theory is simpler than that for continuum states, yet the latter is sufficiently similar that a lot of CNTSHX could be adapted from the corresponding sec-

tions of a well-tested ENESHX. The H_2^+ system provides a particularly clean test of ENESHX by virtue of its non-trivial two-center character, the absence of extraneous physical considerations (like self-consistency or exchange-correlation) and the existence of analytic solutions with exact eigenvalues.²⁵ CNTSHX was then written and used to calculate the total cross sections for photo-ionization of an already doubly ionized lithium atom Li^{2+} for which exact values are also known. (The details of how a single atom can give a suitable test of a molecular program are given below.)

To give more information about the nature of non-MT corrections the programs were constructed to run in three modes, corresponding to the successive introduction of the non-MT parts of the potential. The first, denoted $L=0$, corresponds to the MT version of the potential. The second, denoted $+L > 0$, introduces the higher multipole parts of the potential in the ASR's and the EMR; while the third, denoted $+IR$, then introduces the true nonconstant potential in the IR.

IV. BOUND STATES: THE H_2^+ TEST

We consider the hydrogen molecular ion in the Born-Oppenheimer approximation for fixed proton separation R . The protons are placed on the z axis at $R/2$ and $-R/2$, and each enclosed by a sphere of radius $R/2$ centered on its position. The whole molecule is enclosed by an OS of radius R centered on the origin. We denote this particular partition of space as A. The potential seen by the electron (and also partition A) has point symmetry $D_{\infty h}$ with respect to the origin. From group theory we know that an eigenfunction will transform according to a particular irreducible representation (irrep) of the symmetry group and may be classified accordingly. We search for the ten lowest eigenvalues of the system, which occur in the four irreps A_{1g} , A_{2u} , E_{1g} , and E_{1u} , for $R=2$ a.u. (the equilibrium value).

To investigate the accuracy of the Born approximation that we have used for the IR, we shall revive the idea of Keller⁹ and run the program ENESHX for two further partitions, denoted B and C, which include first one then two sets of interstitial empty spheres, respectively. Details of all three partitions are given in Table I. W and P in Table I stand for wave function and potential and head columns indicating the maximum l value used in the spherical harmonic expansions for these two cases.

In Table II we see the results of our test of ENESHX with the hydrogen molecular ion. Considering first the results of ENESHX for partition A we see that the successive introduction of the non-MT components of the potential gives improved eigenvalues for all ten states. (Note that the differences between the $L=0$ case and the Smith and Johnson values result from our higher partial-wave l_{\max} 's.) Also the relative sizes of the effects of the higher multipole potential components in the ASR's and EMR, and of the nonconstant IR potential, vary among the states. Contrary to a conjecture of Pettifor²⁶ the greater part of the improvement in the $1a_{1g}$ (ground state) level results from the better treatment of the IR potential rather than the higher multipoles in the ASR and EMR potentials. Looking at the $4a_{2u}$ level we note²⁵ that the bulk of the electron density is in the EMR so that even in the $+L > 0$ mode the eigenvalue is exact, showing that the integration of the coupled radial equations for \underline{r} is accurate. Hence we can say that the remaining error in, say, the $1a_{1g}$ level is due to the Born approximation for the IR. This is borne out by the further improvements for the empty-sphere partitions B and C. In B we have a ring of six empty spheres around the "equator" of our earlier partition A, while in C another two rings of six are added above and below the first ring. (The lowering of point symmetry does not split the four irreps that two are considering.) The transfer of some of the IR volume into empty spheres that are treated like atoms (in which the Born approximation is not made) does lead to

TABLE I. Summary of details of partitions used for H_2^+ . For each one is given its point symmetry, with main symmetry axis taken along the z axis. Details of the numbers, positions, and radii of spheres are given together with maximum l values used in potential and wave-function partial-wave expansions, and resulting secular matrix dimensions for each irrep. Partitions are oriented with the xz plane as mirror plane. For IR we show the number of mesh points for numerical quadratures to calculate \underline{T} , together with the amount of OS volume in the IR. Distances are in atomic units.

Molecular partition						A	B	C
Point symmetry						$D_{\infty h}$	D_{6h}	D_{6h}
Group of equivalent spheres used in partition	Numbers of spheres	Radii (a.u.)	Prototype position (x,y,z) (a.u.)	l_{\max}				
				W	P			
	1 (OS)	2	(0,0,0)	6	12	+	+	+
	2 (H)	1	(0,0,1)	3	6	+	+	+
	6	2/3	(4/3, 0,0)	2	4		+	+
	12	2/5	(6/5, 2√3/5, 4/5)	2	4			+
Secular matrix dimension, by irrep								
					A_{1g}	8	13	19
					A_{2u}	7	9	15
					E_{1g}	6	10	19
					E_{1u}	6	13	22
Details of IR		Number of integration mesh points				1830	2790	4710
		Percentage of OS volume				75.0	52.8	43.2

TABLE II. Comparison of the energy eigenvalues (in rydbergs) for H_2^+ from ENESHX (for the three partitions and three program modes) with those from the MT program ENERGY of Smith and Johnson (Ref. 3) and with the exact values calculated analytically (Ref. 25).

State	ENERGY		ENESHX		Exact eigenvalues
	Partition A	$L=0$	Partition A $+L > 0$	+IR	
$1a_{1g}$	-2.0716	-2.07196	-2.10906	-2.18973	-2.20525
$2a_{1g}$	-0.70738	-0.70412	-0.70769	-0.72093	-0.72173
$3a_{1g}$	-0.45574	-0.45597	-0.47330	-0.47102	-0.47155
$4a_{1g}$	-0.34859	-0.34873	-0.35123	-0.35525	-0.35536
$1a_{2u}$	-1.2868	-1.28795	-1.31151	-1.33426	-1.33507
$2a_{2u}$	-0.49722	-0.49752	-0.50696	-0.51085	-0.51083
$3a_{2u}$	-0.26979	-0.26973	-0.27310	-0.27466	-0.27463
$4a_{2u}$	-0.24997	-0.24994	-0.25329	-0.25329	-0.25329
$1e_{1g}$	-0.44646	-0.44646	-0.45397	-0.45333	-0.45340
$1e_{1u}$	-0.88866	-0.88867	-0.86514	-0.85585	-0.85755

State	ENESHX Partition B			ENESHX Partition C		
	$L=0$	$+L > 0$	+IR	$L=0$	$+L > 0$	+IR
$1a_{1g}$	-2.07376	-2.13616	-2.19780	-2.07376	-2.13987	-2.19847
$2a_{1g}$	-0.70426	-0.71198	-0.72123	-0.70425	-0.71221	-0.72119
$3a_{1g}$	-0.45621	-0.47254	-0.47130	-0.45621	-0.47244	-0.47131
$4a_{1g}$	-0.34878	-0.35247	-0.35524	-0.34878	-0.35249	-0.35522
$1a_{2u}$	-1.28385	-1.30953	-1.33406	-1.28384	-1.31165	-1.33425
$2a_{2u}$	-0.49721	-0.50703	-0.51082	-0.49721	-0.50745	-0.51085
$3a_{2u}$	-0.26982	-0.27332	-0.27465	-0.26982	-0.27347	-0.27465
$4a_{2u}$	-0.24999	-0.25332	-0.25329	-0.24999	-0.25331	-0.25329
$1e_{1g}$	-0.44610	-0.45355	-0.45334	-0.44610	-0.45348	-0.45335
$1e_{1u}$	-0.88966	-0.86363	-0.85699	-0.88969	-0.86353	-0.85711

improved eigenvalues, particularly in the $1a_{1g}$ case. As before, for a fixed partition, we get general improvement going from $L=0$ to $+L > 0$ to +IR. Between partitions it is not so uniform and the improvements are, in general, fairly marginal. Clearly, with partition C, a point of diminishing returns has been reached.

V. CONTINUUM STATES AND PHOTOIONIZATION: THE Li^{2+} TEST

Our main interest in the continuum states of a molecule is for their application in calculations of core-level photoionization in the context of x-ray-absorption near-edge structure (XANES). CNTSHX was specially written for this application and it is via the calculation of total photoionization cross section as a function of energy above threshold that we test the FB SW method for continuum states. Unfortunately, no analytic formula for the continuum states of H_2^+ seems to exist. The only formula that we know of is that for hydrogenlike ions, which can be used to calculate cross sections.²⁷ For technical reasons we choose to consider photoionization from the $1s$ ground state of Li^{2+} .

Now this system consists of only one ion with a spherically symmetric potential which may be represented exactly by a MT potential with no IR, and cross sections arbitrarily close to the exact ones obtained. This would not serve our purpose so we make instead a "pseudocluster" in which the central ion (enclosed in a 4-a.u.-radius

sphere) is coordinated by six empty spheres (of radii 1.5 a.u.) in an octahedral configuration and everything enclosed in an OS of radius 7 a.u. In this way the MT approximation is not so good and we might expect to see differences as the non-MT potential components are introduced. In Fig. 1 we see the CNTSHX results for this system.

Firstly, we see that the $+L > 0$ mode gives only slight improvement over the $L=0$ mode (MT case). This is because higher potential multipole components exist only in the empty spheres whose volume is small in comparison with the IR. The inclusion of the influence of the non-constant IR potential produces the main improvement; and above 1 Ry the residual error is reduced to less than 1%. Below 1 Ry it seems reasonable to attribute the error of up to 5% to the Born approximation.

VI. DISCUSSION

Our results indicate that the FP SW theory is fundamentally valid and that our numerical implementation is accurate (and the programs correctly coded). Furthermore, the size of cluster represented (in effect) by partition C for H_2^+ shows that a useful range of molecular types and sizes is accessible even with modest computing resources. It is nevertheless clear that more testing should be done to widen our understanding of the nature and relative importance of non-MT corrections in a variety of circumstances. More, in fact, may be made of

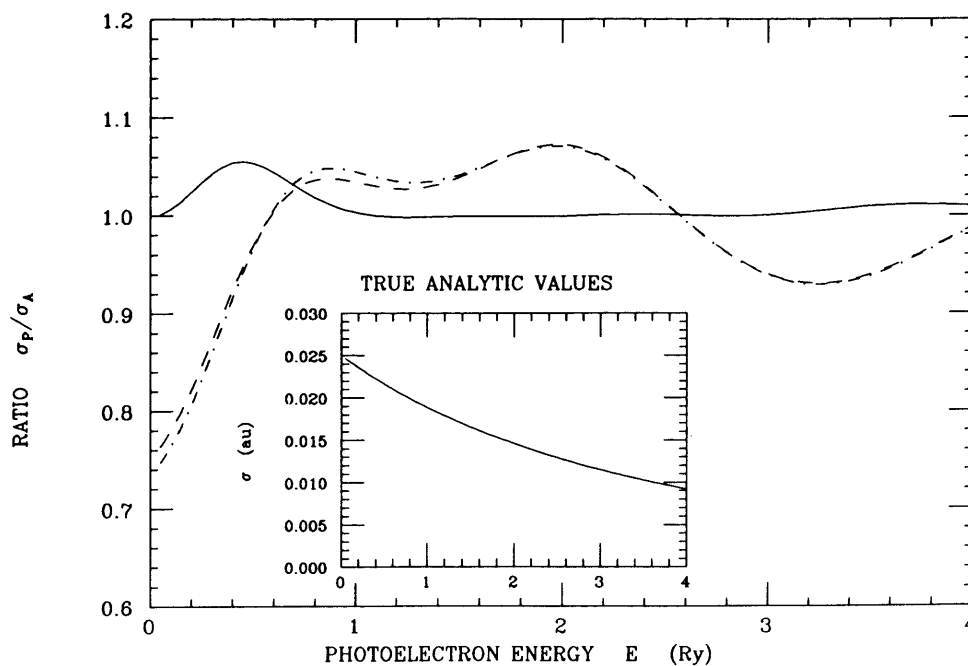


FIG. 1. Comparison (as ratios) of CNTSHX photoionization cross sections for Li^{2+} (for three program modes) with exact analytic values (inset). The solid line represents $+IR$, the dotted-dashed line $L=0$, and the dashed line $+L > 0$.

our present tests. In particular, it would be interesting to have a close look at the effects of non-MT corrections on the spatial variation of wave functions, especially since a lot of important physical quantities are related to matrix elements which involve the wave functions.

At this point we are ready to proceed to calculations for more interesting physical systems. In a subsequent paper we intend to present FP SW results for the Cr K -edge XANES of the model compound chromium hexacarbonyl $\text{Cr}(\text{CO})_6$. For this molecule the MT approximation is particularly bad and non-MT corrections significant. This system is a useful analog, at least from the standpoint of XANES, for important systems such as metal centers in enzymes or some industrial catalysts. In these cases we have no analytic solutions available and the ultimate test is the experimental spectrum. Now,

however, there are other physical processes in operation and it is only by separating out the errors due to the absence of non-MT corrections, as we now can, that we may confidently investigate those due to other deficiencies of the physical model.

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