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Feasibility and Competitiveness of a Reduced Basis Approach for Rapid Electronic Structure Calculations in Quantum Chemistry

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Abstract. We apply the reduced basis methodology to electronic structure calculations with a view to significantly speeding up this computation when it must be performed many times — as in each time step of an ab initio MD simulation or inside a geometry optimization procedure. The feasibility and the efficiency of the approach are demonstrated on several test cases. Promising directions for further research and application to real-scale computations are indicated and discussed.

1. Introduction

As opposed to other more generic problems of the engineering sciences, computational quantum chemistry problems are known to be sufficiently specific to justify a dedicated numerical approach. Indeed, the methods developed over the past sixty years on such problems are very special in nature. This is in particular the case because (*i*) the problems to be addressed are incredibly complex, even when compared with infamous engineering problems of outstanding difficulty; and (*ii*) the methods have been developed by the community of chemists and physicists without almost any real involvement of experts in numerical analysis and scientific computing. Although it is often the case that efficiency is reached at the price of non-genericity, in quantum chemistry the situation is extreme. As a result, there exist many approaches that have proved successful in several engineering domains but which have not been at all tested or adapted in the context of computational chemistry. Reduced basis methods are one instance of such approaches. It is the purpose of the present article to report on some exploratory applications of this general methodology to the specific quantum chemistry context. As will be seen, and although definite conclusions on the validity of the approach on real cases are yet to be obtained, the results are definitely promising and certainly sufficient to motivate further efforts.

Let us briefly give some insight into the mathematical nature of the calculations that are at the heart of a standard quantum chemistry computation. Basically, all quantum chemistry calculations rely on a first central computation: electronic ground state of the physical system under study, a molecular system of finite size or a condensed phase. Excited states predictions, linear response theory calculations, conformations determinations, ab initio molecular dynamics simulations, etc, all rely on this basic foundation. This central computation is a challenge on its own: in principle, being given a set of nuclei (which are typically treated as classical point particles) located at (possibly momentarily) fixed positions in space, the task is to determine the wavefunction corresponding to the electonic ground state; this solves the quantum N-body problem, parameterized by the positions of nuclei. Mathematically, the latter problem is the minimization of a quadratic form on functions varying in $L^2(\mathbb{R}^{3N})$, subject to the constraint that these functions are antisymmetric and appropriately normalized. For almost all physically relevant cases $N \geq 3$, the N-body problem is untractable and thus the dominant strategy in computational chemistry consists in deriving models approximating this N-body problem. These approximated models are in turn discretized and solved numerically.

Hartree-Fock (HF) type models [**34, 6**] and Density Functional Theory (DFT) type models [**8, 25, 6**] are the main two categories of approximation models. They both consist of a non-quadratic constrained

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minimization problem. At the discretized level, it is solved in practice by considering a *nonlinear eigenvalue problem*, which is the specific form of the Euler-Lagrange equation associated with the constrained minimization problem. A solution to this problem is searched for iteratively so as to (hopefully) minimize the energy; the procedure is called the Self-Consistent-Field iteration. The existence of this nonlinear eigenvalue problem at the core of quantum chemistry calculations is the origin of the tremendous overall computational cost of the problem. To realize this, it suffices to recall that in a geometry optimization calculation (i.e., the search for the global minimizer — configuration of nuclei and ground state electronic wavefunction — that minimizes the global energy), or in ab initio molecular dynamics calculations (i.e., the integration in time of the Newton equations of motion for the nuclei equipped with their electronic cloud assumed in its parameterized ground-state) [**10, 19**], each iteration of the search (or of the numerical integrator, as appropriate) involves as the inner loop the solution of this nonlinear eigenvalue problem. There is thus much interest in accelerating this inner loop calculation, and it is a long standing problem of computational chemistry.

What often makes the problem tractable in practice is that the chemists have developed specific case-dependent basis sets which are remarkably efficient. Owing to the very nature of the basis set functions, the size of the matrices is kept sufficiently small so that (at least for systems of up to a hundred of electrons) a solution may be calculated for an acceptable price at excellent accuracy. This is fortunate, because such calculations are very demanding in terms of accuracy.

However, the efficient basis sets developed are often dependent on the positions of the nuclei. They typically correspond to solutions of hydrogenoic-like problems (Slater-type orbitals, ...), or approximations of thereof, developed for the purpose of computational efficiency (contracted Gaussian basis sets, ...). In a situation where the positions of the nuclei vary (and this is the case both in the context of geometry optimization or time-dependent simulations), such basis sets are often delicate and slow to manipulate. They are sometimes replaced by more standard basis sets, independent of the positions of the nuclei, that are less efficient for a fixed configuration of nuclei but more efficient when the latter vary; a typical example is a plane wave basis set. Such basis sets are also typically used for solid phase calculations, where the problem is posed on the unit cell of a lattice and subject to periodic boundary conditions. The efficiency of these more general basis sets comes at a price: the size of the basis set required to reach a good accuracy is then much larger than was the case for nuclei-dependent basis sets.

All of these considerations indicate that, in the context of varying nuclei positions, there is an opportunity for better basis sets to be developed. This motivates the application of the reduced basis methodology. The reduced basis method was first introduced in the late 1970s in the context of nonlinear structural analysis [**1, 24**] and subsequently abstracted, analyzed, and extended to a much larger class of parametrized partial differential equations [**9, 28, 14, 27, 16**]. The foundation of the reduced basis method is built upon three important realizations, which we phrase here in the particular context of quantum chemistry.

The first realization is that in the molecular dynamics simulation of a physical system the quantity of primary importance is typically *not* the field variable u^{e} — such as the wavefunctions or the electron density, but rather certain selected *output of interest* s^{e} — such as the ground state energies of the system and the forces exerted on the nuclei. Both the field variable u^{e} and output s^{e} depend on the parameters, or *inputs*, μ, which serve to identify a particular configuration of the system. Typical inputs include nuclei positions, dimensions of the simulation cells, and the dielectric constant. The relevant system behavior is thus described by an implicit input-output relationship, $s^{\mathrm{e}}(\mu)$, evaluation of which demands solution of the underlying partial differential equation governing electronic structure. In practice, the exact solution $u^{\mathrm{e}}(\mu)$ (respectively, output $s^{\mathrm{e}}(\mu)$) is not available and must thus be replaced by a "truth" approximation $u(\mu)$ (respectively, $s(\mu)$) which resides in a finite dimensional approximation space of dimension $\mathcal{N}$. Nevertheless, as mentioned earlier, calculation of the truth approximation $u(\mu)$ and output $s(\mu)$ can be expensive for certain classes of quantum chemistry problems.

The second realization is related to the choice of basis sets alluded to earlier. The critical observation is that $u(\mu)$ in fact resides on a very low-dimensional manifold $\mathcal{M} \equiv \{u(\mu) | \mu \in \mathcal{D}\}$ induced by the parametric dependence; here $\mathcal{D} \in \mathbb{R}^P$ is the parameter space in which our input μ — a P-tuple of parameters — varies. Furthermore, the field variable $u(\mu)$ will often be quite regular in μ — the parametrically induced manifold $\mathcal{M}$ is smooth — even when the field variable enjoys only limited regularity with respect to the spatial coordinate.[1] The reduced basis method explicitly recognizes and exploits dimension reduction afforded by the low-dimensional — and smooth — parametrically induced solution manifold. More precisely, rather than general basis sets such as the plane wave basis set, the basis set consists of solutions of the partial differential equation at N^u selected parameter points $\mu_i, 1 \leq i \leq N^u$. Then, the set of all solutions $u(\mu)$ as μ varies can be approximated very well by its projection on a finite and low dimensional vector space spanned by the $u(\mu_i)$: for sufficiently well chosen μ_i, there exist coefficients $c_i, 1 \leq i \leq N(\mu)$ such that the finite sum $\sum_{i=1}^{N^u} c_i u(\mu_i)$ is very close to $u(\mu)$ for any μ.

The third realization lies in what we term the "computational opportunities". Here, we rely on two observations. The first observation derives from the mathematical formulation: very often, the partial differential operator can be expressed as the sum of Q products of (known, easily evaluated) parameter-*dependent* functions and parameter-*independent* operators; we shall denote this structure as "affine" parameter dependence. The second observation derives from our context: molecular dynamic simulation requires rapid and repetitive evaluations of the "input-output" relations and thus places a predominant emphasis on very low *marginal* cost — the additional effort associated with each new evaluation. These two observations present a clear investment-amortization opportunity: we can exploit the underlying affine parametric structure to design effective *offline-online* computational procedures which willingly accept greatly increased initial preprocessing — offline — expense in exchange for greatly reduced marginal — online — "in service" cost.

In the more recent past the reduced-basis approach and in particular associated *a posteriori* error estimation procedures have been successfully developed for (i) linear elliptic and parabolic PDEs that are affine in the parameter [**20, 21, 29, 37, 13**] ; and (ii) elliptic PDEs that are at most quadratically nonlinear in the first argument [**36, 23, 35**]. In these cases a very efficient offline-online computational strategy can be developed. The operation count for the online stage — in which, given a new parameter value, we calculate the reduced-basis output and associated error bound — depends only on N^u (typically small) and Q, but it is *independent* of $\mathcal{N}$, the dimension of the underlying "truth" approximation.

Unfortunately, in quantum chemistry computations based on Hartree-Fock type models or Density Functional Theory type models, the underlying PDEs do not have the same nice structure that allows us to apply the methodology developed in earlier work. There are three main issues: (i) the equations can contain both non-affine terms and also very nasty nonlinear terms, for example associated with an exchange-correlation term; (ii) the solution sought is not scalar — for each μ, we look for a a set of eigensolutions; and (iii) the parameterizations of the PDEs can be complex, for example due to a set of moving nuclei and periodic boundary conditions. In fact, the above three issues are the main difficulties faced by any numerical approximation of the PDEs obtained in computational chemistry and are the deciding factors when determining the appropriate numerical approach to employ. From this particular mathematical standpoint, Hartree-Fock type models and Density Functional Theory type models are, with all due respect, similar.

In this paper, we will address theses issues albeit in an idealized "model" context. In Section 2, we review the recently developed "empirical interpolation procedure" [**2, 12**] through a simple model elliptic problem. Then in Section 3 and Section 4, we apply the approach within the quantum chemistry context: in Section 3 to a (non-affine) HF hydrogen molecular system; and in Section 4 to a (nonlinear) DFT one-dimensional model. Section 3 also addresses, or at least introduces, issues of geometric and parametric complexity. And Section 4 proposes a "solution" to the many-electron difficulty. We will not handle issues related to *a posteriori* error estimators in this paper, but they are essential to our overall reduced-basis methodology and will be addressed in our future work.

Note that our reduced-basis approximation is built (offline) upon the "truth" approximation; in subsequent sections, the "truth" approximation is based on the finite element approximation. The choice is purely for convenience; certainly there are other and better choices — and hence any discussions of offline effort are, at best, notional. We could in fact use other basis sets; in [**26**], the planewave method is the choice of "truth" approximation.

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[1] The smoothness is deduced from the equation for the sensitivity derivatives; the stability and continuity properties of the partial differential operator are crucial. Clearly the latter are a delicate matter in the context of eigenvalue problems.

2. Methodology

2.1. Abstract Formulation. To simplify our presentation, we will describe our methodology based on a nonlinear elliptic problem. Extensions to nonlinear eigenvalue problems of interest in quantum chemistry will be discussed in subsequent sections. The abstract statement of the nonlinear elliptic problem is as follows: given any $\mu \in \mathcal{D} \subset \mathbb{R}^P$, we evaluate the output $s^{\mathrm{e}}(\mu)$ as

$$s^{\mathrm{e}}(\mu) = \ell(u^{\mathrm{e}}(\mu)) \tag{2.1}$$

where $u^{\mathrm{e}}(\mu) \in Y^{\mathrm{e}}$ is the solution of

$$\mu a_0(u^{\mathrm{e}}(\mu), v) + \int_\Omega g(u^{\mathrm{e}}(\mu); x; \mu) v = f(v), \quad \forall v \in Y^{\mathrm{e}}. \tag{2.2}$$

Here $\mathcal{D}$ is the parameter domain in which our P-tuple (input) parameter μ resides (here $P = 1$); $Y^{\mathrm{e}}(\Omega)$ is an appropriate Hilbert space with the associated inner product $(w, v)_{Y^{\mathrm{e}}} = \int_\Omega \nabla w \cdot \nabla v + wv$ and norm $|| \cdot ||_{Y^{\mathrm{e}}} = (\cdot, \cdot)_Y^{1/2}$; Ω is a bounded domain in $\mathbb{R}^d$ with Lipschitz continuous boundary $\partial\Omega$; $g(w; x; \mu)$ is a general nonaffine nonlinear function of $w \in Y$, spatial coordinate x, and the parameter μ; $a_0(\cdot, \cdot)$ is a Y^{e}-continuous bilinear functional; and $f(\cdot)$ and $l(\cdot)$ are Y^{e}-continuous linear functionals. These functionals are not parameter-dependent. Our function space $Y^{\mathrm{e}}(\Omega)$ will satisfy $(H_0^1(\Omega))^\nu \subset Y^{\mathrm{e}}(\Omega) \subset (H^1(\Omega))^\nu \subset (L^2(\Omega))^\nu$, where $\nu = 1$ for a scalar field variable and $\nu = d$ for a vector field variable. Here $H^1(\Omega)$ (respectively, $H_0^1(\Omega)$) is the usual Hilbert space of derivative square-integrable functions (respectively, derivative square-integrable functions that vanish on the domain boundary $\partial\Omega$) and $L^2(\Omega)$ is the Lebesgue space of square-integrable functions [**30**].

More often than not, the exact solution is not available and we thus replace $u^{\mathrm{e}}(\mu)$ with a "truth" approximation, $u(\mu)$, which resides in (say) a suitably fine piecewise-linear finite element approximation space $Y \subset Y^{\mathrm{e}}$ of *very* large dimension $\mathcal{N}$. The abstract statement for the resulting problem is thus: given any $\mu \in \mathcal{D}$, we evaluate $s(\mu) = \ell(u(\mu))$, where $u(\mu) \in Y$ satisfies

$$\mu a_0(u(\mu), v) + \int_\Omega g(u(\mu); x; \mu) v = f(v), \quad \forall v \in Y. \tag{2.3}$$

We shall assume — hence the appellation "truth" — that the discretization is sufficiently rich such that $u(\mu)$ and $u^{\mathrm{e}}(\mu)$ and hence $s(\mu)$ and $s^{\mathrm{e}}(\mu)$ are indistinguishable at the accuracy level of interest. The reduced-basis approximation shall be built upon this reference (or "truth") finite element approximation, and the error of this approximation will thus be evaluated with respect to $u(\mu) \in Y$. Our formulation must be stable and efficient as $\mathcal{N} \to \infty$. Note that Y inherits the inner product and norm from Y^{e}.

We shall make the following assumptions. First, we assume that the bilinear form $a_0(\cdot, \cdot) : Y \times Y \to \mathbb{R}$ is symmetric, $a_0(w, v) = a_0(v, w), \forall\, w, v \in Y$. We shall also make two crucial hypotheses related to well-posedness. Our first hypothesis is that the bilinear form a_0 satisfies the following stability and continuity conditions:

$$0 < \alpha \equiv \inf_{v \in Y} \frac{\mu a_0(v, v)}{\|v\|_Y^2}, \quad \forall \mu \in \mathcal{D}\ , \tag{2.4}$$

$$\sup_{w \in Y} \sup_{v \in Y} \frac{\mu a_0(w, v)}{\|w\|_Y \|v\|_Y} \equiv \gamma < \infty, \quad \forall \mu \in \mathcal{D}, \tag{2.5}$$

and that $f \in L^2(\Omega)$. In the second hypothesis, we require $g : \mathbb{R} \times \Omega \times \mathcal{D} \to \mathbb{R}$ to be continuous in its arguments, increasing in its first argument, and $g(z; x; \mu) \geq 0$, $\forall z \in \mathbb{R}$, $\forall x \in \Omega$ and $\forall \mu \in \mathcal{D}$. With these assumptions, the problems (2.2) and (2.3) are then well-posed [**12**].

2.2. Reduced-Basis Approximation.

2.2.1. *Empirical Interpolation Procedure.* We first introduce the nested samples, $S_N^u = \{\mu_1^u \in \mathcal{D}, \ldots, \mu_N^u \in \mathcal{D}\}$, $1 \leq N \leq N_{\max}$, and associated nested Lagrangian [**28**] reduced-basis spaces $W_N^u = \mathrm{span}\{u(\mu_n^u),\ 1 \leq n \leq N\} = \mathrm{span}\ \{\zeta_n,\ 1 \leq n \leq N\}$, $1 \leq N \leq N_{\max}$, where $u(\mu_n^u)$ is the solution of (2.2) at $\mu = \mu_n^u$ and $\zeta_n, 1 \leq n \leq N$ are the orthonormalized bases of $u(\mu_n^u)$, $1 \leq n \leq N$ with respect to $(\cdot,\cdot)_Y$. The classical reduced-basis approximation [**20, 21, 29, 37, 13**] is then obtained by a standard Galerkin projection: given $\mu \in \mathcal{D}$, we evaluate

$$s_N(\mu) = \ell(u_N(\mu)) \ , \tag{2.6}$$

where $u_N(\mu) \in W_N^u$ satisfies

$$\mu a_0(u_N(\mu), v) + \int_\Omega g(u_N(\mu); x; \mu) \ v = f(v), \quad \forall v \in W_N^u. \tag{2.7}$$

Unfortunately, the presence of *strong* nonlinearity in g does not allow an efficient *offline-online* procedure outlined in [**36, 23**]. As a result, although the dimension of the system (2.7) is small, solving it is actually expensive: the evaluation of the nonlinearity term $\int_\Omega g(u_N(\mu); x; \mu) v$ will scale as some power of $\mathcal{N}$. Due to this $O(\mathcal{N})$ dependence, it is somewhat disingenuous to interpret (2.7) as a reduced-order model since the resulting computational advantage relative to classical approaches using advanced iterative techniques can be modest.

Our goal is to efficiently compute $s_N(\mu)$ such that the incurred computational cost is dependent on the dimension of reduced-basis approximation spaces and the parametric complexity of the problems, but *independent* of $\mathcal{N}$. Towards this end, we develop a collateral reduced-basis expansion for the nonlinear term by using the empirical interpolation procedure [**2, 12**] reviewed below.

In particular, we consider the approximation of the parameter-dependent nonlinear function $g(w; x; \mu)$ by a reduced-basis expansion $g_M^w(x; \mu)$ based upon the empirical interpolation procedure outlined in [**2, 12**]. The procedure includes three steps. In the first step, we introduce nested samples $S_M^g = \{\mu_1^g \in \mathcal{D}, \dots, \mu_M^g \in \mathcal{D}\}, 1 \le M \le M_{\max}$ and associated nested approximation spaces $W_M^g = \operatorname{span}\{\xi_m \equiv g(u(x; \mu_m^g); x; \mu_m^g), 1 \le m \le M\}$. The construction of S_M^g and W_M^g is based on a greedy selection process. We first define the best approximation $g_M^*(x;\mu) \equiv \arg\min_{z \in W_M^g} \|g(u(x;\mu_m^g); \ \cdot\ ; \mu) - z\|_{L^\infty(\Omega)}$ and the associated error $\varepsilon_M^*(\mu) \equiv \|g(u(x;\mu_m^g); \ \cdot\ ;\mu) - g_M^*(\ \cdot\ ;\mu)\|_{L^\infty(\Omega)}$. Then, we choose our first sample point to be $\mu_1^g = \arg\max_{\mu \in \Xi^g} \|g(\ \cdot\ ;\ \cdot\ ;\mu)\|_{L^\infty(\Omega)}$, and define $S_1^g = \{\mu_1^g\}$, $\xi_1(x) \equiv g(u(x;\mu_1^g); x; \mu_1^g)$, and $W_1^g = \operatorname{span}\{\xi_1\}$; here Ξ^g is a suitably large but finite-dimensional parameter set in $\mathcal{D}$. For $M \ge 2$, we determine $\mu_M^g = \arg\max_{\mu \in \Xi^g} \varepsilon_{M-1}^*(\mu)$, and define $S_M^g = S_{M-1}^g \cup \mu_M^g$, $\xi_M(x) = g(u(x;\mu_M^g); x; \mu_M^g)$, and $W_M^g = \operatorname{span}\{\xi_m, 1 \le m \le M\}$. In essence, W_M^g comprises basis functions from the parametrically induced manifold $\mathcal{M}^g \equiv \{g(u(\ \cdot\ ;\mu);\ \cdot\ ;\mu) \mid \mu \in \mathcal{D}\}$.[2]

In the second step, we construct nested sets of interpolation points $T_M = \{t_1, \dots, t_M\}$, $1 \le M \le M_{\max}$. We first set $t_1 = \arg\operatorname{ess\,sup}_{x \in \Omega} |\xi_1(x)|$, $q_1(x) = \xi_1(x)/\xi_1(t_1)$, $B_{11}^1 = 1$. Then for $M = 2, \dots, M_{\max}$, we solve the linear system $\sum_{j=1}^{M-1} \sigma_j^{M-1} q_j(t_i) = \xi_M(t_i)$, $1 \le i \le M-1$, and set $r_M(x) = \xi_M(x) - \sum_{j=1}^{M-1} \sigma_j^{M-1} q_j(x)$, $x_M = \arg\operatorname{ess\,sup}_{x \in \Omega} |r_M(x)|$, $q_M(x) = r_M(x)/r_M(t_M)$, and $B_{i\,j}^M = q_j(t_i)$, $1 \le i, j \le M$.

Finally, for any given $w \in Y$ and M, we may approximate $g(w; x; \mu)$ by $g_M^w(x;\mu) = \sum_{m=1}^M \varphi_{M\,m}(\mu) q_m(x)$, where $\sum_{j=1}^M B_{i\,j}^M \varphi_{M\,j}(\mu) = g(w(t_i); t_i; \mu)$, $1 \le i \le M$ and $B_{i\,j}^M = q_j(t_i)$. Although this "composed" interpolant is defined for general $w \in Y$, we expect good approximation only for w (very) close to the manifold $\mathcal{M}^u \equiv \{u(\mu) \mid \mu \in \mathcal{D}\}$ on which W_M^g is constructed. Theoretical and numerical aspects of the empirical interpolation have been analyzed in great detail in [**2, 12**]. We summarize here the main results: (*i*) the process is stable — B^M is a well-conditioned lower triangular matrix with dominant unity diagonal; and (*ii*) $\varepsilon_M(\mu) \le \varepsilon_M^*(\mu)(1 + \Lambda_M)$, where $\varepsilon_M(\mu) = ||g(u(\cdot;\mu);\cdot;\mu) - g_M^{u(\mu)}(\cdot;\mu)||_{L^\infty}$ [**2, 12**] and the Lebesgue constant, Λ_M, is bounded above by $2^M - 1$.[3]

We may now replace $g(u_N(\mu); x; \mu)$ — as required in our reduced-basis projection for $u_N(\mu)$ — with $g_M^{u_{N,M}}(x;\mu)$. Our reduced-basis approximation is thus: given $\mu \in \mathcal{D}$, we evaluate

$$s_{N,M}(\mu) = \ell(u_{N,M}(\mu)) \ , \tag{2.8}$$

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[2] Thanks to our truth approximation, the optimization for $g_{M-1}^*(x;\mu)$ and hence $\varepsilon_{M-1}^*(\mu)$ is a *standard linear program.* In actual practice, rather than the $L^\infty(\Omega)$-norm, we exploit the $L^2(\Omega)$-norm surrogate in our best approximation, the construction of S_M^g is considerably less expensive.

[3] The bound is very pessimistic and of little practical value. In applications, the actual asymptotic behavior of the Lebesgue constant is much lower than the upper bound $2^M - 1$, typically $O(M)$; however, the bound does provide a theoretical basis for some stability.

where $u_{N,M}(\mu) \in W_N^u$ satisfies

$$\mu a_0(u_{N,M}(\mu), v) + \int_\Omega g_M^{u_{N,M}}(x;\mu) v = f(v), \quad \forall\, v \in W_N^u \ . \tag{2.9}$$

As shown in the next subsection, this reduced-basis formulation enables us to develop a very efficient *offline-online* procedure for the computation of $s_{N,M}(\mu)$.

Finally, we address the issue related to the choice of our parameter samples S_N^u and thus the corresponding reduced-basis spaces W_N^u. We could in fact generalize the greedy selection process outlined in Section 2.2.1 for the construction of any S_N^u [**29, 36, 23**]. We assume that we are given a sample S_N^u and hence reduced-basis space W_N^u and associated reduced-basis approximation (procedure to determine) $u_{N,M}(\mu)$ and $s_{N,M}(\mu)$, $\forall \mu \in \mathcal{D}$. Then, for a suitably fine grid Ξ_{Test} over the parameter space $\mathcal{D}$, we determine $\mu_N^* = \arg\max_{\mu \in \Xi_{\text{Test}}} \varepsilon_{N,M}^u(\mu)$ and append μ_N^* to S_N^u to form S_{N+1}^u and hence W_{N+1}^u. There is considerable flexibility in the definition of $\varepsilon_{N,M}^u(\mu)$, the measure of the approximation error — for example, we may use

$$\text{error in } s_{N,M}(\mu) \quad : \quad |s_{N,M}(\mu) - s(\mu)|, \tag{2.10}$$

$$\text{error in } u_{N,M}(\mu) \quad : \quad ||u_{N,M}(\mu) - u(\mu)||_Y, \tag{2.11}$$

$$\text{projection error} \quad : \quad \min_{\nu \in \mathbb{R}^N} || \sum_{n=1}^N \nu_n \zeta_n - u(\mu)||_Y. \tag{2.12}$$

The procedure is repeated until $\max_{\mu \in \Xi_{\text{Test}}} \varepsilon_{N,M}^u(\mu)$ is below a tolerance we desire. In essence, this strategy ensure "maximally independent" snapshots and hence a rapidly convergent reduced-basis approximation. This, in conjunction with our orthogonalization procedure, also guarantees a well-conditioned reduced-basis discrete system. This strategy is clearly not very effective in high-dimensional parameter spaces, as it requires solutions of (2.3) at all parameter points in Ξ_{Test}. Note however that if a rigorous *a posteriori* error estimator is available, a more efficient procedure is possible [**29, 23**].

2.2.2. *Offline–Online Procedure.* We now demonstrate how the incorporation of the empirical interpolation method into the reduced-basis approximation leads to an efficient *online–offline* computational strategy. To see this more clearly, we expand our reduced-basis approximation and empirical interpolation approximation as

$$u_{N,M}(\mu) = \sum_{j=1}^N u_{N,M\,j}(\mu)\zeta_j \ , \qquad g_M^{u_{N,M}}(x;\mu) = \sum_{m=1}^M \varphi_{M\,m}(\mu) q_m(x) \ . \tag{2.13}$$

Inserting these representations into (2.9) yields

$$\mu \sum_{j=1}^N A_{i\,j}^N u_{N,M\,j}(\mu) + \sum_{m=1}^M C_{i\,m}^{N,M} \varphi_{M\,m}(\mu) = F_{N\,i}, \quad 1 \le i \le N \ ; \tag{2.14}$$

where $A^N \in \mathbb{R}^{N\times N}, C^{N,M} \in \mathbb{R}^{N\times M}, F_N \in \mathbb{R}^N$ are given by $A_{i\,j}^N = a_0(\zeta_j, \zeta_i), 1 \le i,j \le N$, $C_{i\,m}^{N,M} = \int_\Omega q_m \zeta_i, 1 \le i \le N, 1 \le m \le M$, and $F_{N\,i} = f(\zeta_i), 1 \le i \le N$, respectively. Furthermore, $\varphi_M(\mu) \in \mathbb{R}^M$ is given by

$$\begin{aligned} \sum_{k=1}^M B_{m\,k}^M \varphi_{M\,k}(\mu) &= g(u_{N,M}(t_m;\mu); t_m; \mu), \quad 1 \le m \le M \\ &= g\Big(\sum_{n=1}^N u_{N,M\,n}(\mu)\zeta_n(t_m); t_m; \mu\Big), \quad 1 \le m \le M \ . \end{aligned} \tag{2.15}$$

We then substitute $\varphi_M(\mu)$ from (2.15) into (2.14) to obtain the following nonlinear algebraic system

$$\mu \sum_{j=1}^N A_{i\,j}^N u_{N,M\,j}(\mu) + \sum_{m=1}^M D_{i\,m}^{N,M} g\Big(\sum_{n=1}^N \zeta_n(t_m) u_{N,M\,n}(\mu); t_m; \mu\Big) = F_{N\,i}, \quad 1 \le i \le N \ , \tag{2.16}$$

where $D^{N,M} = C^{N,M}(B^M)^{-1} \in \mathbb{R}^{N\times M}$.

To solve (2.16) for $u_{N,M\,j}(\mu), 1 \le j \le N$, we may apply a Newton iterative scheme: given a current iterate $\bar{u}_{N,M\,j}(\mu), 1 \le j \le N$, we must find an increment $\delta u_{N,M\,j}, 1 \le j \le N$, such that

$$\sum_{j=1}^{N} \left(\mu A^N_{i\,j} + \bar{E}^N_{i\,j}\right) \delta u_{N,M\,j}(\mu) = F_{N\,i} - \mu \sum_{j=1}^{N} A^N_{i\,j} \bar{u}_{N,M\,j}(\mu) - \sum_{m=1}^{M} D^{N,M}_{i\,m}\, g\Big(\sum_{n=1}^{N} \zeta_n(t_m) \bar{u}_{N,M\,n}(\mu); t_m; \mu\Big), \quad 1 \le i \le N \ ; \tag{2.17}$$

here $\bar{E}^N \in \mathbb{R}^{N \times N}$ must be calculated at every Newton iteration as

$$\bar{E}^N_{i\,j} = \sum_{m=1}^{M} D^{N,M}_{i\,m}\, g'\Big(\sum_{n=1}^{N} \zeta_n(t_m) \bar{u}_{N,M\,n}(\mu); t_m; \mu\Big) \zeta_j(t_m), \quad 1 \le i, j \le N \ , \tag{2.18}$$

where $g'(w; t; \mu)$ is the first derivative of g with respect to w. Finally, the output can be evaluated as

$$s_{N,M}(\mu) = \sum_{j=1}^{N} u_{N,M\,j}(\mu) L_{N\,j} \ , \tag{2.19}$$

where $L_N \in \mathbb{R}^N$ is the output vector with entries $L_{N\,j} = \ell(\zeta_j), 1 \le j \le N$. We observe that we can now develop an efficient *offline-online* procedure for the rapid evaluation of $s_{N,M}(\mu)$ for each μ in $\mathcal{D}$.

In the offline stage — performed once — we generate nested reduced-basis spaces $W^u_N = \{\zeta_1, \ldots, \zeta_N\}, 1 \le N \le N_{\max}$, nested approximation spaces $W^g_M = \{q_1, \ldots, q_M\}, 1 \le M \le M_{\max}$, and nested sets of interpolation points $T_M = \{t_1, \ldots, t_M\}$; we then form and store $A^N, B^M, D^{N,M}$, and F_N. In the online stage — performed many times for each new μ — we solve (2.17) for $u_{N,M\,j}(\mu), 1 \le j \le N$. The operation count of the online stage is essentially the predominant Newton update component: at each Newton iteration, we first assemble the right-hand side and compute $\bar{E}^N$ at cost $O(MN^2)$ — note we perform the sum in the parenthesis of (2.18) before performing the outer sum; we then form and invert the left-hand side (Jacobian) at cost $O(N^3)$. The online complexity depends only on N, M and number of Newton iterations; we thus recover online $\mathcal{N}$ independence.

2.3. A Simple Example. We consider a particular instantiation of our abstract statement in which

$$a_0(w, v) = \int_\Omega \nabla w \cdot \nabla v, \qquad f(v) = \int_\Omega v, \qquad g(w) = |w|^{2/3} w, \tag{2.20}$$

and $\ell = f$; here $\Omega =]0, 1[\in \mathbb{R}$, w and $v \in Y \equiv H^1_0(\Omega)$, and $\mu \in \mathcal{D} \equiv [0.001, 1]$. Our model problem is clearly well-posed. In addition, small μ results in boundary layer solutions as shown in Figure 1.

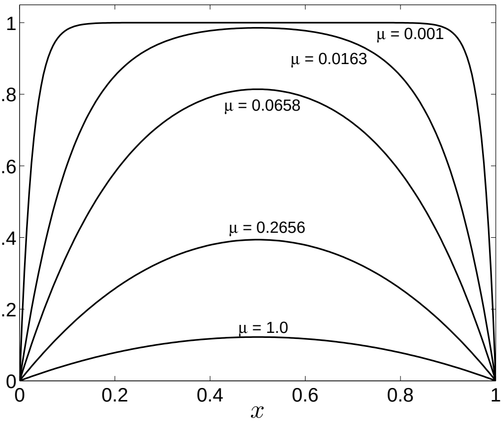


FIGURE 1. Solution $u(\mu)$ for several values of μ.

We now present numerical results for the reduced-basis approximation. To begin, we introduce a parameter sample $\Xi_{\rm Test} \subset \mathcal{D}$ of size 100 and define $\varepsilon^s_{N,M} = \max_{\mu \in \Xi_{\rm Test}} |s(\mu) - s_{N,M}(\mu)|/|s(\mu)|$. We show in Figure 2 convergence of $\varepsilon^s_{N,M}$ with respect to N and M. We observe that the reduced-basis approximation converges very rapidly. In addition, the quality of our reduced-basis approximation depends on N and M in a strongly coupled manner: for a fixed value of M, the error decreases monotonically with N for $N \le N_M$, where N_M is such that there is no appreciable change in $\varepsilon^s_{N,M}$ for $N > N_M$. However, when M is increased, the achievable $\varepsilon^s_{N,M}$ decreases further and N_M increases; this strongly suggests that the reduced-basis error is strongly limited by the error in the initial construction of our empirical interpolation approximation.

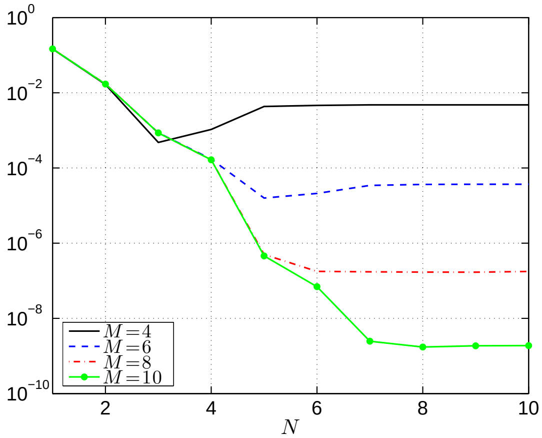


FIGURE 2. Convergence of the maximum relative error $\varepsilon^s_{N,M}$ as a function of N and M.

3. Hydrogen Molecule

In this section, we use the reduced-basis method to rapidly determine the ground state energy of a hydrogen molecule. We then demonstrate the computational savings afforded by our reduced-basis approximation in a molecular dynamics (MD) simulation of the hydrogen molecule. Although the hydrogen molecule is the simplest multi-electron molecule, numerical calculation of its properties was the first demonstration of the power of the Schrödinger equation in quantum chemistry.

3.1. Problem Description.

3.1.1. *Exact Statement.* We consider the interaction of an hydrogen molecular system consisting of a pair of electrons and two nuclei, each with effectively infinite mass and charge $Z = 1$. The positions of the nuclei in the Cartesian coordinates r are denoted by $R_i, i = 1, 2$, those of the electrons are denoted by $r_i, i = 1, 2$, and the internuclear separation is denoted by R. Then, the Hamiltonian of this molecular system reads as

$$\mathbf{H} = -\sum_{i=1}^{2} \left(\frac{\nabla_i^2}{2} + \sum_{j=1}^{2} \frac{Z}{|r_i - R_j|} \right) + \frac{1}{|r_1 - r_2|} + \frac{Z^2}{R} \ , \tag{3.1}$$

for which the ground state solution is described by a ground-state wavefunction $\psi^{\rm e}$. By applying the Born-Oppenheimer approximation and the restricted Hartree-Fock (RHF) theory [**34, 15, 6, 18, 17**], which expresses the wavefunction as the determinant of two single-electron wavefunctions with similar spatial component, we obtain the RHF problem: the ground-state molecular orbital $\mathcal{U}^{\rm e}$ is given by

$$\mathcal{U}^{\rm e} = \arg \inf_{w \in H^1(\mathbb{R}^3)} \left\{ E^{\rm e}_{\rm RHF}(w), \quad \int_{\mathbb{R}^3} w^2 dr = 1 \right\} \ , \tag{3.2}$$

where the energy $E^{\rm e}_{\rm RHF}(w)$ is given by

$$E^{\rm e}_{\rm RHF}(w) = \frac{1}{2} \int_{\mathbb{R}^3} |\nabla w|^2 dr - \int_{\mathbb{R}^3} \frac{w^2}{|r - R_1|} dr - \int_{\mathbb{R}^3} \frac{w^2}{|r - R_2|} dr + \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{w^2(r) w^2(r')}{|r - r'|} dr' dr \ . \tag{3.3}$$

Recall that $H^1(\mathbb{R}^3)$ is the Hilbert space in $\mathbb{R}^3$. For any $w \in H^1(\mathbb{R}^3)$, let

$$\Phi(w) = \int_{\mathbb{R}^3} \frac{w^2(r')}{|r-r'|} dr' \ , \tag{3.4}$$

it thus follows that $\Phi(w)$ is the solution of the Poisson problem

$$-\nabla^2 \Phi(w) = 4\pi w^2 \quad \text{in } \mathbb{R}^3 \ . \tag{3.5}$$

We shall exploit this potential in what follows.

To further simplify (3.2), we exploit the symmetry of the solution $\mathcal{U}^{\rm e}$ and recast the problem into an infinite half-plane $\mathbb{R}^2_+$; we denote the axial and radial coordinates as y_1 and y_2, respectively. Let the origin of the coordinate system be the midpoint between the two nuclei; the positions of the two nuclei are thus $(-\mu/2, 0)$ and $(\mu/2, 0)$. Here, $\mu \equiv R$, the internuclear separation, is the only parameter of interest, and varies in the range $\mathcal{D} \equiv [0.5, 6]$. By introducing $u^{\rm e}_\infty(y) = \sqrt{2\pi}\mathcal{U}^{\rm e}(y), \forall y = (y_1, y_2) \in \mathbb{R}^2_+$, we can rewrite the above RHF problem as

$$u^{\rm e}_\infty(y;\mu) = \arg \inf_{w \in H^1_0(\mathbb{R}^2_+)} \left\{ E^{\rm e}_\infty(w;\mu), \quad \int_{\mathbb{R}^2_+} w^2 y_2 dy_1 dy_2 = 1 \right\} \ . \tag{3.6}$$

Here the energy functional $E^{\rm e}_\infty(w;\mu)$ is given by

$$E^{\rm e}_\infty(w;\mu) = \frac{1}{2}\int_{\mathbb{R}^2_+} |\nabla w|^2 y_2 dy_1 dy_2 - \int_{\mathbb{R}^2_+} g_{\rm o}(y;\mu) w^2 dy_1 dy_2 + \frac{1}{2}\int_{\mathbb{R}^2_+} \phi^{\rm e}_\infty w^2 y_2 dy_1 dy_2 \ , \tag{3.7}$$

where

$$g_{\rm o}(y;\mu) = \frac{y_2}{\sqrt{(y_1+\mu/2)^2 + y_2^2}} + \frac{y_2}{\sqrt{(y_1-\mu/2)^2 + y_2^2}} \ , \tag{3.8}$$

$$-\nabla^2 \phi^{\rm e}_\infty = 2w^2 \quad \text{in } \mathbb{R}^2_+ \ . \tag{3.9}$$

The boundary conditions for both $u^{\rm e}_\infty$ and $\phi^{\rm e}_\infty$ are homogeneous Neumman on $y_2 = 0$ and homogeneous Dirichlet at infinity.

We next truncate the infinite half-plane domain to a large parameter-dependent computational domain $\Omega_{\rm o}(\mu) \equiv]-25-\mu/2, 25+\mu/2[\times]0, 25[$ as shown in Figure 3(a); since the largest possible value of μ is $6 \ll 25$, $\Omega_{\rm o}$ is sufficiently large that the truncation will not adversely affect our solution. As a result, the RHF problem for the hydrogen molecular system is being approximated by

$$u^{\rm e}_{\rm o}(y;\mu) = \arg \inf_{w \in H^1_0(\Omega_{\rm o}(\mu))} \left\{ E^{\rm e}_{\rm o}(w;\mu), \quad \int_{\Omega_{\rm o}(\mu)} w^2 y_2 dy_1 dy_2 = 1 \right\} \ , \tag{3.10}$$

where

$$E^{\rm e}_{\rm o}(w;\mu) = \frac{1}{2}\int_{\Omega_{\rm o}(\mu)} |\nabla w|^2 y_2 dy_1 dy_2 - \int_{\Omega_{\rm o}(\mu)} g_{\rm o}(y;\mu) w^2 dy_1 dy_2 + \frac{1}{2}\int_{\Omega_{\rm o}(\mu)} \phi^{\rm e}_{\rm o} w^2 y_2 dy_1 dy_2 \ , \tag{3.11}$$

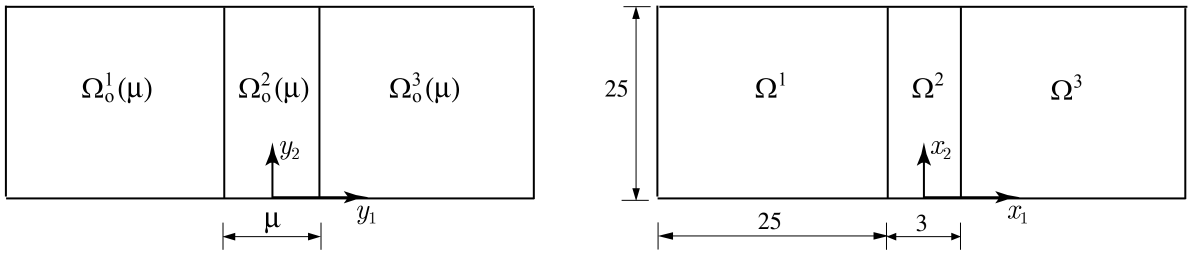
$$-\nabla^2 \phi^{\rm e}_{\rm o} = 2w^2 \quad \text{in } \Omega_{\rm o}(\mu) \ . \tag{3.12}$$

The outputs of interest are $s^{\rm e}_{\rm o}(\mu) = E^{\rm e}_{\rm o}(u^{\rm e}_{\rm o}(\mu);\mu)$ and $\partial s^{\rm e}_{\rm o}(\mu)/\partial\mu = \partial E^{\rm e}_{\rm o}(u^{\rm e}_{\rm o}(\mu);\mu)/\partial\mu$ from which we may calaculate the ground state energy of the hydrogen molecular system $\mathcal{E}^{\rm e}_{{\rm o}\,{\rm H}_2}(\mu) = 2s^{\rm e}_{\rm o}(\mu) + 1/\mu$ and the force exerted on the nuclei, $F^{\rm e}_{{\rm o}\,{\rm H}_2}(\mu) = 2\partial s^{\rm e}_{\rm o}(\mu)/\partial\mu - 1/\mu^2$. The boundary conditions for both $u^{\rm e}_{\rm o}$ and $\phi^{\rm e}_{\rm o}$ are homogeneous Neumman on $y_2 = 0$ and homogeneous Dirichlet on the rest of the boundary.

3.1.2. *Mapped Formulation on Reference Domain.* We next introduce a reference domain $\Omega = \Omega_{\rm o}(\mu = 3) =]-26.5, 26.5[\times]0, 25[$ as shown in Figure 3(b). We decompose $\Omega_{\rm o}(\mu)$ and Ω as

$$\overline{\Omega}_{\rm o}(\mu) = \overline{\Omega}^1_{\rm o}(\mu) \cup \overline{\Omega}^2_{\rm o}(\mu) \cup \overline{\Omega}^3_{\rm o}(\mu), \quad \overline{\Omega} = \overline{\Omega}^1 \cup \overline{\Omega}^2 \cup \overline{\Omega}^3 \ , \tag{3.13}$$

where $\Omega^1_{\rm o}(\mu) \equiv]-25-\mu/2, -\mu/2[\times]0, 25[$, $\Omega^2_{\rm o}(\mu) \equiv]-\mu/2, \mu/2[\times]0, 25[$, $\Omega^3_{\rm o}(\mu) \equiv]\mu/2, 25+\mu/2[\times]0, 20[$, $\Omega^1 \equiv]-26.5, -1.5[\times]0, 25[$, $\Omega^2 \equiv]-1.5, 1.5[\times]0, 25[$, $\Omega^3 \equiv]1.5, 26.5[\times]0, 25[$. We now consider a piecewise affine mapping $\mathcal{F}$ from Ω to $\Omega_{\rm o}(\mu)$: the mapping is $(y_1, y_2) = (x_1 + 1.5 - \mu/2, x_2)$ from Ω^1 to $\Omega^1_{\rm o}(\mu)$; the mapping is $(y_1, y_2) = (\frac{\mu}{3}x_1, x_2)$ from Ω^2 to $\Omega^2_{\rm o}(\mu)$; the mapping is $(y_1, y_2) = (x_1 - 1.5 + \mu/2, x_2)$ from Ω^3 to $\Omega^3_{\rm o}(\mu)$.



(a) (b)

FIGURE 3. Truncated computational domains: (a) original domain, and (b) reference domain.

Our exact solution on the original domain, $u_{\rm o}^{\rm e}(y;\mu)$, can then be expressed in terms of the solution on the mapped domain, $u^{\rm e}(x;\mu)$, as $u_{\rm o}^{\rm e}(y;\mu) = u^{\rm e}(\mathcal{F}^{-1}(y);\mu)$. The solution on the mapped domain, $u^{\rm e}(x;\mu) \in Y^{\rm e} \equiv H_0^1(\Omega)$ satisfies

$$u^{\rm e}(x;\mu) = \arg \inf_{w\in Y^{\rm e}} \{E^{\rm e}(w;\mu), \quad m(w,w;\mu) = 1\} \ , \tag{3.14}$$

where

$$E^{\rm e}(w;\mu) = \frac{1}{2}a_0(w,w;\mu) - a(w,w;g(x;\mu)) + \frac{1}{2}b(w,w,\phi^{\rm e}(w);\mu) \ , \tag{3.15}$$

$$a_0(\phi^{\rm e}(w),v;\mu) = 2b(w,w,v;\mu), \quad \forall\ v \in Y^{\rm e}\ . \tag{3.16}$$

Here the forms are given by

$$a_0(w,v;\mu) = \int_{\Omega^1} \nabla w \nabla v x_2 dx_1 dx_2 + \frac{3}{\mu}\int_{\Omega^2} \frac{\partial w}{\partial x_1}\frac{\partial v}{\partial x_1} x_2 dx_1 dx_2 + \frac{\mu}{3}\int_{\Omega^2} \frac{\partial w}{\partial x_2}\frac{\partial v}{\partial x_2} x_2 dx_1 dx_2 + \int_{\Omega^3} \nabla w \nabla v x_2 dx_1 dx_2 \tag{3.17}$$

$$m(w,v;\mu) = \int_{\Omega^1} wvx_2 dx_1 dx_2 + \frac{\mu}{3}\int_{\Omega^2} wvx_2 dx_1 dx_2 + \int_{\Omega^3} wvx_2 dx_1 dx_2 \tag{3.18}$$

$$b(w,v,z;\mu) = \int_{\Omega^1} wvzx_2 dx_1 dx_2 + \frac{\mu}{3}\int_{\Omega^2} wvzx_2 dx_1 dx_2 + \int_{\Omega^3} wvzx_2 dx_1 dx_2 \tag{3.19}$$

$$a(w,v;g(x;\mu)) = a_1(w,v;g_1(x;\mu)) + a_2(w,v;g_2(x;\mu)) + a_3(w,v;g_3(x;\mu)) \tag{3.20}$$

where

$$\begin{aligned} a_1(w,v;g_1(x;\mu)) &= \int_{\Omega^1} g_1(x;\mu) wv dx_1 dx_2 \\ a_2(w,v;g_2(x;\mu)) &= \int_{\Omega^2} g_2(x;\mu) wv dx_1 dx_2 \\ a_3(w,v;g_3(x;\mu)) &= \int_{\Omega^3} g_3(x;\mu) wv dx_1 dx_2 \end{aligned}$$

and

$$g(x;\mu) = \begin{cases} g_1(x;\mu) = \frac{x_2}{\sqrt{(x_1+1.5)^2+x_2^2}} + \frac{x_2}{\sqrt{(x_1+1.5-\mu)^2+x_2^2}}, & x \in \Omega_1\ , \\ g_2(x;\mu) = \frac{\mu}{3}\frac{x_2}{\sqrt{\left(\frac{\mu}{3}x_1+\frac{\mu}{2}\right)^2+x_2^2}} + \frac{\mu}{3}\frac{x_2}{\sqrt{\left(\frac{\mu}{3}x_1-\frac{\mu}{2}\right)^2+x_2^2}}, & x \in \Omega_2 \\ g_3(x;\mu) = \frac{x_2}{\sqrt{(x_1-1.5+\mu)^2+x_2^2}} + \frac{x_2}{\sqrt{(x_1-1.5)^2+x_2^2}}, & x \in \Omega_3\ . \end{cases}$$

Our outputs of interest are then evaluated as $s^{\rm e}(\mu) = E^{\rm e}(u^{\rm e}(\mu);\mu)$ and $\partial s^{\rm e}(\mu)/\partial\mu = \partial E^{\rm e}(u^{\rm e}(\mu);\mu)/\partial\mu$. In this reference domain, the ground state energy of the hydrogen molecular system is then given by $\mathcal{E}_{\rm H_2}^{\rm e}(\mu) = 2s^{\rm e}(\mu) + 1/\mu$ and the force exerted on the nuclei is given by $F_{\rm H_2}^{\rm e}(\mu) = 2\partial s^{\rm e}(\mu)/\partial\mu - 1/\mu^2$.

3.1.3. *Truth Approximation.* We now introduce the "truth" approximations $u(\mu) \in Y$ and $\phi(\mu) \in Y$, where $Y \subset Y^{\mathrm{e}}$ is a truth linear finite approximation space of dimension $\mathcal{N}$. By application of the Euler-Lagrange formulation, we obtain a generalized nonlinear eigenvalue system for $(u(\mu), \phi(\mu), \lambda(\mu)) \in Y \times Y \times \mathbb{R}$ given by

$$\frac{1}{2}a_0(u(\mu), v; \mu) - a(u(\mu), v; g(x; \mu)) + b(\phi(\mu), u(\mu), v; \mu) = \lambda(\mu) m(u(\mu), v; \mu), \quad \forall v \in Y \ , \tag{3.21}$$

$$\frac{1}{2}a_0(\phi(\mu), v; \mu) = b(u(\mu), u(\mu), v; \mu), \quad \forall v \in Y \ , \tag{3.22}$$

$$m(u(\mu), u(\mu); \mu) = 1 \ . \tag{3.23}$$

Here $\lambda(\mu)$ is the Lagrange multiplier. It then follows that $s(\mu) = \lambda(\mu) - \frac{1}{2}b(\phi(\mu), u(\mu), u(\mu); \mu)$, and after simple algebraic manipulations, we obtain

$$\begin{aligned}\partial s(\mu)/\partial\mu = \frac{1}{2}a_0'(u(\mu), u(\mu); \mu) - a'(u(\mu), u(\mu); g(x; \mu)) + b'(\phi(\mu), u(\mu), u(\mu); \mu) \\ - \lambda(\mu) m'(u(\mu), u(\mu); \mu) - \frac{1}{4}a_0'(\phi(\mu), \phi(\mu); \mu) \ ;\end{aligned} \tag{3.24}$$

where the prime denotes the partial derivative of the forms with respect to the parameter μ. The ground state energy of the hydrogen molecular system is then given by $\mathcal{E}_{\mathrm{H}_2}(\mu) = 2s(\mu) + 1/\mu$ and the force exerted on the nuclei is given by $F_{\mathrm{H}_2}(\mu) = 2\partial s(\mu)/\partial\mu - 1/\mu^2$.

The Newton's method is then used to solve the above system: given a current iterate $(\bar{u}(\mu), \bar{\phi}(\mu), \bar{\lambda}(\mu)) \in Y \times Y \times \mathbb{R}$, we find an increment $(\delta u(\mu), \delta\phi(\mu), \delta\lambda(\mu)) \in Y \times Y \times \mathbb{R}$ such that

$$\begin{aligned}\frac{1}{2}a_0(\delta u(\mu), v; \mu) - a(\delta u(\mu), v; g(x; \mu)) + b(\bar{\phi}(\mu), \delta u(\mu), v; \mu) - \bar{\lambda}(\mu) m(\delta u(\mu), v; \mu) + b(\delta\phi(\mu), \bar{u}(\mu), v; \mu) \\ -\delta\lambda(\mu) m(\bar{u}(\mu), v; \mu) &= \bar{\lambda}(\mu) m(\bar{u}(\mu), v; \mu) - \frac{1}{2}a_0(\bar{u}(\mu), v; \mu) + a(\bar{u}(\mu), v; g(x; \mu)) \\ &\quad -b(\bar{\phi}(\mu), \bar{u}(\mu), v; \mu), \quad \forall v \in Y \ , \\ b(\delta u(\mu), \bar{u}(\mu), v; \mu) - \frac{1}{4}a_0(\delta\phi(\mu), v; \mu) &= \frac{1}{4}a_0(\bar{\phi}(\mu), v; \mu) - \frac{1}{2}b(\bar{u}(\mu), \bar{u}(\mu), v; \mu), \quad \forall v \in Y \ , \\ m(\delta u(\mu), \bar{u}(\mu); \mu) &= \frac{1}{2}(1 - m(\bar{u}(\mu), \bar{u}(\mu); \mu)) \ .\end{aligned}$$

To accelerate the convergence, the already computed solution at a particular parameter $\mu = \mu_{\mathrm{old}}$ is taken as an initial guess when solving the system for $\mu = \mu_{\mathrm{new}}$.

3.2. Reduced-Basis Formulation. We realize that the problem is nonlinear in $u(\mu)$ and $\phi(\mu)$ and nonaffine in μ. Since the nonlinearity is only quadratic, the nonlinear terms can be efficiently treated by the usual reduced-basis formulation [**13, 23, 35**]. To achieve an economical reduced-basis approximation of $\mathcal{N}$-*independent* online complexity, however, the empirical interpolation method is needed to deal with the nonaffine terms.

3.2.1. *Discrete Equations.* To begin, we introduce two samples $S^u_{N^u} = \{\mu^u_1, \ldots, \mu^u_{N^u}\}$ and $S^\phi_{N^\phi} = \left\{\mu^\phi_1, \ldots, \mu^\phi_{N^\phi}\right\}$ and two associated reduced-basis approximation spaces $W^u_{N^u} = \text{span}\left\{\zeta_j \equiv u(\mu^u_j), 1 \le j \le N^u\right\}$ and $W^\phi_{N^\phi} = \text{span}\left\{\varsigma_j \equiv \phi(\mu^\phi_j), 1 \le j \le N^\phi\right\}$. We next construct three samples $S^{g_1}_{M^{g_1}} = \{\mu^{g_1}_1, \ldots, \mu^{g_1}_{M^{g_1}}\}$, $S^{g_2}_{M^{g_2}} = \{\mu^{g_2}_1, \ldots, \mu^{g_2}_{M^{g_2}}\}$, and $S^{g_3}_{M^{g_3}} = \{\mu^{g_3}_1, \ldots, \mu^{g_3}_{M^{g_3}}\}$; associated approximation spaces $W^{g_1}_{M^{g_1}} = \text{span}$ $\{g_1(x; \mu^{g_1}_j),\ 1 \le j \le M^{g_1}\} = \text{span}\ \{q^{g_1}_1, \ldots, q^{g_1}_{M^{g_1}}\}$, $W^{g_2}_{M^{g_2}} = \text{span}\left\{g_2(x; \mu^{g_2}_j), 1 \le j \le M^{g_2}\right\} = \text{span}\ \{q^{g_2}_1$, $\ldots$, $q^{g_2}_{M^{g_2}}\}$, and $W^{g_3}_{M^{g_3}} = \text{span}\left\{g_3(x; \mu^{g_3}_j), 1 \le j \le M^{g_3}\right\} = \text{span}\{q^{g_3}_1, \ldots, q^{g_3}_{M^{g_3}}\}$; and three sets of interpolations points $T^{g_1}_{M^{g_1}} = \{t^{g_1}_1, \ldots, t^{g_1}_{M^{g_1}}\}$, $T^{g_2}_{M^{g_2}} = \{t^{g_2}_1, \ldots, t^{g_2}_{M^{g_2}}\}$, $T^{g_3}_{M^{g_3}} = \{t^{g_3}_1, \ldots, t^{g_3}_{M^{g_3}}\}$ following the empirical interpolation procedure outlined in Section 2.2.1. For simplicity of exposition, throughout this section we assume that $N^\phi = N^u \equiv N$ and $M^{g_1} = M^{g_2} = M^{g_3} \equiv M$.

By applying a standard Galerkin projection and replacing the nonaffine functions $g_1(x; \mu)$, $g_2(x; \mu)$, and $g_3(x; \mu)$ with our coefficient function approximations $g_{1M}(x; \mu)$, $g_{2M}(x; \mu)$, and $g_{3M}(x; \mu)$, we obtain the reduced-basis formulation: given $\mu \in \mathcal{D}$, we evaluate

$$s_{N,M}(\mu) = \lambda_{N,M}(\mu) - \frac{1}{2} b(\phi_{N,M}(\mu), u_{N,M}(\mu), u_{N,M}(\mu); \mu) \ , \tag{3.25}$$

and

$$\begin{aligned} \frac{\partial s_{N,M}(\mu)}{\partial \mu} = \frac{1}{2} a_0'(u_{N,M}(\mu), u_{N,M}(\mu); \mu) - a_1'(u_{N,M}(\mu), u_{N,M}(\mu); g_{1M}(x;\mu)) - a_2'(u_{N,M}(\mu), u_{N,M}(\mu); g_{2M}(x;\mu)) \\ - a_3'(u_{N,M}(\mu), u_{N,M}(\mu); g_{3M}(x;\mu)) + b'(\phi_{N,M}(\mu), u_{N,M}(\mu), u_{N,M}(\mu); \mu) \\ - \lambda(\mu) m'(u_{N,M}(\mu), u_{N,M}(\mu); \mu) - \frac{1}{4} a_0'(\phi_{N,M}(\mu), \phi_{N,M}(\mu); \mu) \ ; \end{aligned} \tag{3.26}$$

where $(u_{N,M}(\mu), \phi_{N,M}(\mu), \lambda_{N,M}(\mu)) \in W_N^u \times W_N^\phi \times \mathbb{R}$ is the solution of

$$\begin{aligned} \frac{1}{2} a_0(u_{N,M}(\mu), v; \mu) - a_1(u_{N,M}(\mu), v; g_{1M}(x;\mu)) - a_2(u_{N,M}(\mu), v; g_{2M}(x;\mu)) - a_3(u_{N,M}(\mu), v; g_{3M}(x;\mu)) & \\ + b(\phi_{N,M}(\mu), u_{N,M}(\mu), v; \mu) &= \lambda_{N,M}(\mu) m(u_{N,M}(\mu), v; \mu), \quad \forall v \in W_N^u, & (3.27) \\ \frac{1}{2} a_0(\phi_{N,M}(\mu), v; \mu) &= b(u_{N,M}(\mu), u_{N,M}(\mu), v; \mu), \quad \forall v \in W_N^\phi, & (3.28) \\ m(u_{N,M}(\mu), u_{N,M}(\mu); \mu) &= 1 \ . & (3.29) \end{aligned}$$

Here $g_{1M}(x;\mu)$, $g_{2M}(x;\mu)$, and $g_{3M}(x;\mu)$ are given by

$$g_{1M}(x;\mu) = \sum_{m=1}^{M} \beta_m^{g_1}(\mu) q_m^{g_1}(x), \quad g_{2M}(x;\mu) = \sum_{m=1}^{M} \beta_m^{g_2}(\mu) q_m^{g_2}(x), \quad g_{3M}(x;\mu) = \sum_{m=1}^{M} \beta_m^{g_3} q_m^{g_3}(x) \ , \tag{3.30}$$

where, for $j = 1, \dots, M$,

$$\sum_{m=1}^{M} q_m^{g_1}(t_j^{g_1}) \beta_m^{g_1}(\mu) = g_1(t_j^{g_1};\mu), \quad \sum_{m=1}^{M} q_m^{g_2}(t_j^{g_2}) \beta_m^{g_2}(\mu) = g_2(t_j^{g_2};\mu), \quad \sum_{m=1}^{M} q_m^{g_3}(t_j^{g_3}) \beta_m^{g_3}(\mu) = g_3(t_j^{g_3};\mu) \ . \tag{3.31}$$

The reduced-basis approximation to the ground state energy of the hydrogen molecular system is then given by $\mathcal{E}_{N,M\,\mathrm{H}_2}(\mu) = 2 s_{N,M}(\mu) + 1/\mu$ and the reduced-basis approximation to the force exerted on the nuclei is given by $F_{N,M\,\mathrm{H}_2}(\mu) = 2\partial s_{N,M}(\mu)/\partial\mu - 1/\mu^2$. It remains to address the computational complexity of the reduced-basis approximation.

3.2.2. *Offline-Online Procedure.* We first expand our reduced-basis approximations $u_{N,M}(\mu)$ and $\phi_{N,M}(\mu)$ as

$$u_{N,M}(\mu) = \sum_{j=1}^{N} u_{N,M\,j}(\mu) \zeta_j, \quad \phi_{N,M}(\mu) = \sum_{j=1}^{N} \phi_{N,M\,j}(\mu) \varsigma_j \ . \tag{3.32}$$

Inserting these representations and the coefficient-function approximations from (3.30) into (3.27)-(3.29) yields

$$\begin{aligned} \frac{1}{2} \sum_{j=1}^{N} \left\{ a_0(\zeta_j, \zeta_i; \mu) - \sum_{m=1}^{M} \left(\beta_m^{g_1}(\mu) a_1(\zeta_j, \zeta_i; q_m^{g_1}) + \beta_m^{g_2}(\mu) a_2(\zeta_j, \zeta_i; q_m^{g_2}) + \beta_m^{g_3}(\mu) a_3(\zeta_j, \zeta_i; q_m^{g_3}) \right) \right\} u_{N,M\,j}(\mu) & \\ + \sum_{j=1}^{N} \sum_{k=1}^{N} b(\varsigma_j, \zeta_k, \zeta_i; \mu) \phi_{N,M\,j}(\mu) u_{N,M\,k}(\mu) &= \lambda_{N,M}(\mu) \sum_{j=1}^{N} m(\zeta_j, \zeta_i; \mu) u_{N,M\,j}(\mu), \quad 1 \le i \le N, \\ \frac{1}{2} \sum_{j=1}^{N} a_0(\varsigma_j, \varsigma_i; \mu) \phi_{N,M\,j}(\mu) &= \sum_{j=1}^{N} \sum_{k=1}^{N} b(\zeta_j, \zeta_k, \varsigma_i; \mu) u_{N,M\,j}(\mu) u_{N,M\,k}(\mu), \quad 1 \le i \le N, \\ \sum_{j=1}^{N} \sum_{k=1}^{N} m(\zeta_j, \zeta_k; \mu) u_{N,M\,j}(\mu) u_{N,M\,k}(\mu) &= 1 \ . \end{aligned}$$

In a similar fashion as described in Section 2.2.2, this algebraic nonlinear system of $2N+1$ equations can be readily solved by the Newton's method for $u_{N,M\,j}(\mu)$, $\phi_{N,M\,j}(\mu)$, $1 \le j \le N$, and $\lambda_{N,M}(\mu)$. The reduced-basis outputs can then be calculated as

$$s_{N,M}(\mu) = \lambda_{N,M}(\mu) - \frac{1}{2}\sum_{k=1}^{N}\sum_{j=1}^{N}\sum_{i=1}^{N} \phi_{N,M\,k}(\mu) u_{N,M\,j}(\mu) u_{N,M\,i}(\mu) b(\varsigma_k, \zeta_j, \zeta_i; \mu) \ , \tag{3.33}$$

and

$$\begin{aligned} \frac{\partial s_{N,M}}{\partial \mu}(\mu) = \sum_{j=1}^{N}\sum_{i=1}^{N} & u_{N,M\,j}(\mu) u_{N,M\,i}(\mu) \Big(\frac{1}{2} a_0'(\zeta_j, \zeta_i; \mu) - \lambda(\mu) m'(\zeta_j, \zeta_i; \mu) \\ & - \sum_{m=1}^{M} \big(\beta_m^{g_1\prime}(\mu) a_1(\zeta_j, \zeta_i; q_m^{g_1}) + \beta_m^{g_2\prime}(\mu) a_2(\zeta_j, \zeta_i; q_m^{g_2}) + \beta_m^{g_3\prime}(\mu) a_3(\zeta_j, \zeta_i; q_m^{g_3}) \big) \\ & + \sum_{k=1}^{N} \phi_{N,M\,k}(\mu) b'(\varsigma_k, \zeta_j, \zeta_i; \mu) \Big) - \frac{1}{4} \sum_{j=1}^{N}\sum_{i=1}^{N} \phi_{N,M\,j}(\mu) \phi_{N,M\,i}(\mu) a_0'(\varsigma_j, \varsigma_i; \mu) \ , \end{aligned} \tag{3.34}$$

where $\beta_m^{g_1\prime}(\mu)$, $\beta_m^{g_2\prime}(\mu)$, and $\beta_m^{g_3\prime}(\mu)$ are obtained from

$$\sum_{m=1}^{M} q_m^{g_1}(t_j^{g_1}) \beta_m^{g_1\prime}(\mu) = g_1'(t_j^{g_1}; \mu), \quad \sum_{m=1}^{M} q_m^{g_2}(t_j^{g_2}) \beta_m^{g_2\prime}(\mu) = g_2'(t_j^{g_2}; \mu), \quad \sum_{m=1}^{M} q_m^{g_3}(t_j^{g_3}) \beta_m^{g_3\prime}(\mu) = g_3'(t_j^{g_3}; \mu) \ . \tag{3.35}$$

For efficient computation, we employ the offline-online computational strategy.

Towards this end, we may express (3.17)-(3.20) as

$$a_0(\zeta_j, \zeta_i; \mu) = \int_{\Omega^1 \cup \Omega^3} \nabla \zeta_j \nabla \zeta_i x_2 dx_1 dx_2 + \frac{3}{\mu} \int_{\Omega^2} \frac{\partial \zeta_j}{\partial x_1} \frac{\partial \zeta_i}{\partial x_1} x_2 dx_1 dx_2 + \frac{\mu}{3} \int_{\Omega^2} \frac{\partial \zeta_j}{\partial x_2} \frac{\partial \zeta_i}{\partial x_2} x_2 dx_1 dx_2 \tag{3.36}$$

$$a_0(\varsigma_j, \varsigma_i; \mu) = \int_{\Omega^1 \cup \Omega^3} \nabla \varsigma_j \nabla \varsigma_i x_2 dx_1 dx_2 + \frac{3}{\mu} \int_{\Omega^2} \frac{\partial \varsigma_j}{\partial x_1} \frac{\partial \varsigma_i}{\partial x_1} x_2 dx_1 dx_2 + \frac{\mu}{3} \int_{\Omega^2} \frac{\partial \varsigma_j}{\partial x_2} \frac{\partial \varsigma_i}{\partial x_2} x_2 dx_1 dx_2 \tag{3.37}$$

$$b(\varsigma_k, \zeta_j, \zeta_i; \mu) = \int_{\Omega^1 \cup \Omega^3} \varsigma_k \zeta_j \zeta_i x_2 dx_1 dx_2 + \frac{\mu}{3} \int_{\Omega^2} \varsigma_k \zeta_j \zeta_i x_2 dx_1 dx_2 \tag{3.38}$$

$$m(\zeta_j, \zeta_i; \mu) = \int_{\Omega^1 \cup \Omega^3} \zeta_j \zeta_i x_2 dx_1 dx_2 + \frac{\mu}{3} \int_{\Omega^2} \zeta_j \zeta_i x_2 dx_1 dx_2 \tag{3.39}$$

$$a_1(\zeta_j, \zeta_i; q_m^{g_1}) = \int_{\Omega^1} q_m^{g_1} \zeta_j \zeta_i dx_1 dx_2 \tag{3.40}$$

$$a_2(\zeta_j, \zeta_i; q_m^{g_2}) = \int_{\Omega^2} q_m^{g_2} \zeta_j \zeta_i dx_1 dx_2 \tag{3.41}$$

$$a_3(\zeta_j, \zeta_i; q_m^{g_3}) = \int_{\Omega^3} q_m^{g_3} \zeta_j \zeta_i dx_1 dx_2 \tag{3.42}$$

$$a_0'(\zeta_j, \zeta_i; \mu) = -\frac{3}{\mu^2} \int_{\Omega^2} \frac{\partial \zeta_j}{\partial x_1} \frac{\partial \zeta_i}{\partial x_1} x_2 dx_1 dx_2 + \frac{1}{3} \int_{\Omega^2} \frac{\partial \zeta_j}{\partial x_2} \frac{\partial \zeta_i}{\partial x_2} x_2 dx_1 dx_2 \tag{3.43}$$

$$a_0'(\varsigma_j, \varsigma_i; \mu) = -\frac{3}{\mu^2} \int_{\Omega^2} \frac{\partial \varsigma_j}{\partial x_1} \frac{\partial \varsigma_i}{\partial x_1} x_2 dx_1 dx_2 + \frac{1}{3} \int_{\Omega^2} \frac{\partial \varsigma_j}{\partial x_2} \frac{\partial \varsigma_i}{\partial x_2} x_2 dx_1 dx_2 \tag{3.44}$$

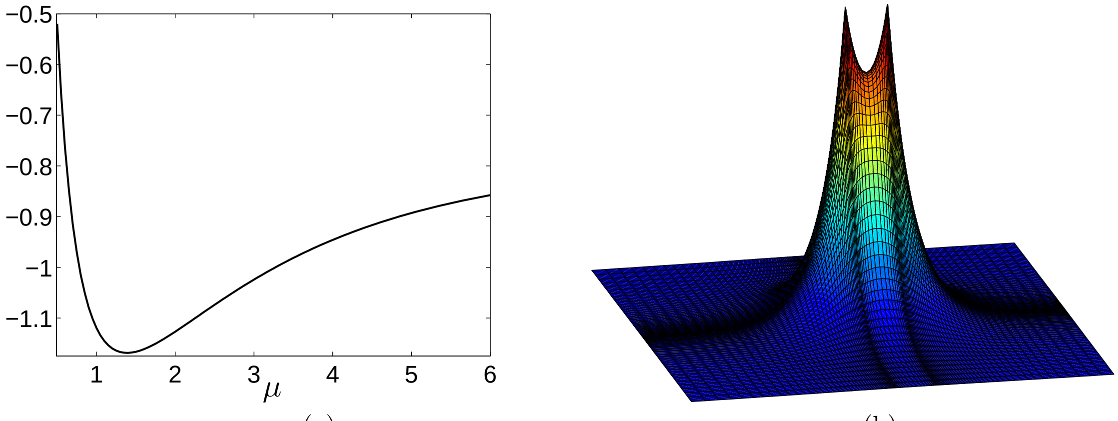
$$b'(\varsigma_k, \zeta_j, \zeta_i; \mu) = \frac{1}{3} \int_{\Omega^2} \varsigma_k \zeta_j \zeta_i x_2 dx_1 dx_2 \tag{3.45}$$

$$m'(\zeta_j, \zeta_i; \mu) = \frac{1}{3} \int_{\Omega^2} \zeta_j \zeta_i x_2 dx_1 dx_2 \ . \tag{3.46}$$

It should now be clear that we can develop an efficient offline-online procedure for the rapid evaluation of $s_{N,M}(\mu)$ and $\partial s_{N,M}(\mu)/\partial\mu$ for each μ in $\mathcal{D}$.

The operation count of the online stage is essentially the predominant Newton update component: at each Newton iteration, we first assemble the right-hand side and form the Jacobian matrix at a cost of $O(2N^3)$ (for a linear problem the scaling would be $O(2N^2)$ — the quadratic terms introduces another factor of N); we then invert the Jacobian matrix at cost $O((2N+1)^3)$. Note that we solve for $\beta_m^{g_1}(\mu)$, $\beta_m^{g_2}(\mu)$, $\beta_m^{g_3}(\mu)$, $\beta_m^{g_1}{}'(\mu)$, $\beta_m^{g_2}{}'(\mu)$, $\beta_m^{g_3}{}'(\mu)$ at cost $O(6M^2)$ by appealing to the triangular property of B^M and form the *affine* parameter-dependent quantities and their partial derivatives at cost $O(3MN^2+N^3)$ *before* pursuing the Newton steps. In summary, the operation count of the online stage is $O(6M^2+K(2N+1)^3)$, where K is the number of Newton iterations. The online complexity is thus *independent* of $\mathcal{N}$.

3.3. Numerical Results. We first present in Figure 4(a) the finite element calculation of the ground state energy of the hydrogen molecular system $\mathcal{E}_{\mathrm{H}_2}$ as a function of the internuclear separation μ for the truth linear finite element approximation of dimension $\mathcal{N}=8601$. The minimum binding energy is -1.1687 and the equilibrium internuclear separation, μ, is 1.4; this is in good agreement with the calculated binding energy of -1.1745 and the calculated equilibrium internuclear separation of 1.4 given in [**33**]. Figure 4(b) shows the wavefunction $u(\mu)$ at the equilibrium internuclear separation.



(a) (b)

FIGURE 4. (a) $\mathcal{E}_{\mathrm{H}_2}$ as a function of μ, and (b) $u(\mu)$ at the equilibrium internuclear separation $\mu=1.4$.

We next introduce a parameter sample $\Xi_{\mathrm{Test}}\subset\mathcal{D}$ of size 111 and define $\varepsilon^s_{N,M}=\max_{\mu\in\Xi_{\mathrm{Test}}}|s(\mu)-s_{N,M}(\mu)|/|s(\mu)|$, $\varepsilon^{ds}_{N,M}=\max_{\mu\in\Xi_{\mathrm{Test}}}|\partial s(\mu)/\partial\mu-\partial s_{N,M}(\mu)/\partial\mu|/|\partial s(\mu)/\partial\mu|$, and $\varepsilon^{\lambda}_{N,M}=\max_{\mu\in\Xi_{\mathrm{Test}}}|\lambda(\mu)-\lambda_{N,M}(\mu)|/|\lambda(\mu)|$. We present in Figure 5 $\varepsilon^s_{N,M}$ as a function of N and M. We observe very rapid convergence of the reduced-basis approximation. Again, we note that the "plateau" in the curves for M fixed and the "drop" in the $N\to\infty$ asymptotes as M increases: for fixed M the error in our coefficient function approximation $g_M(x;\mu)$ to $g(x;\mu)$ will ultimately dominate at large N; increasing M renders the coefficient function approximation more accurate, which in turn leads to the drops in the asymptotic error. We tabulate in Table 1 $\varepsilon^s_{N,M}$, $\varepsilon^{ds}_{N,M}$, and $\varepsilon^{\lambda}_{N,M}$ for different values of N and M. We observe that the reduced-basis outputs converge very rapidly and that, as expected, $s_{N,M}(\mu)$ and $\lambda_{N,M}(\mu)$ converge faster than $\partial s_{N,M}/\partial\mu(\mu)$. Indeed, it is clear from Figure 5 that we can further reduce the errors in Table 1 by using larger M.

We now present in Table 2 the online computational times to calculate $\partial s_{N,M}/\partial\mu(\mu)$ as a function of N and M; the values are normalized with respect to the computational time for the direct calculation of the truth approximation output $\partial s/\partial\mu(\mu)$. We achieve significant computational savings: for a relative accuracy of close to 0.1 percent (corresponding to $N=M=10$ in Table 1) in the output, the online saving is more than a factor of 5000 relative to the FEM. Of course, when competing with more efficient quantum chemistry methods particularly developed for solution of the RHF problems, the computational savings will be not really that great. Nevertheless, the reduced-basis approach does provide an attractive alternative to

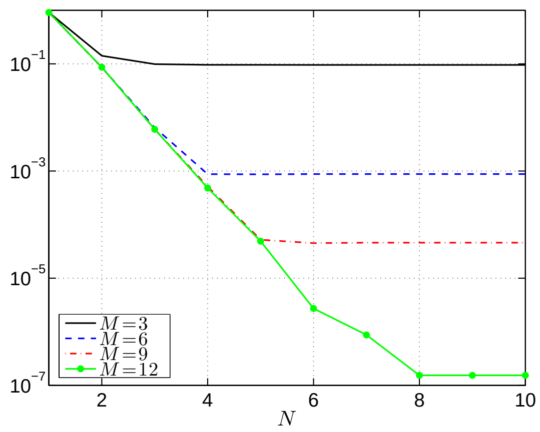


FIGURE 5. Convergence of the maximum error $\varepsilon^{s}_{N,M}$ as a function of N and M.

N	M	$\varepsilon^{s}_{N,M}$	$\varepsilon^{ds}_{N,M}$	$\varepsilon^{\lambda}_{N,M}$
2	2	1.17 E − 01	1.18 E − 00	1.72 E − 01
4	4	3.94 E − 02	5.86 E − 01	3.88 E − 02
6	6	8.76 E − 04	4.29 E − 02	1.11 E − 03
8	8	6.37 E − 05	6.98 E − 03	6.17 E − 05
10	10	8.30 E − 06	1.07 E − 03	1.07 E − 05
12	12	1.54 E − 07	3.96 E − 06	4.75 E − 07

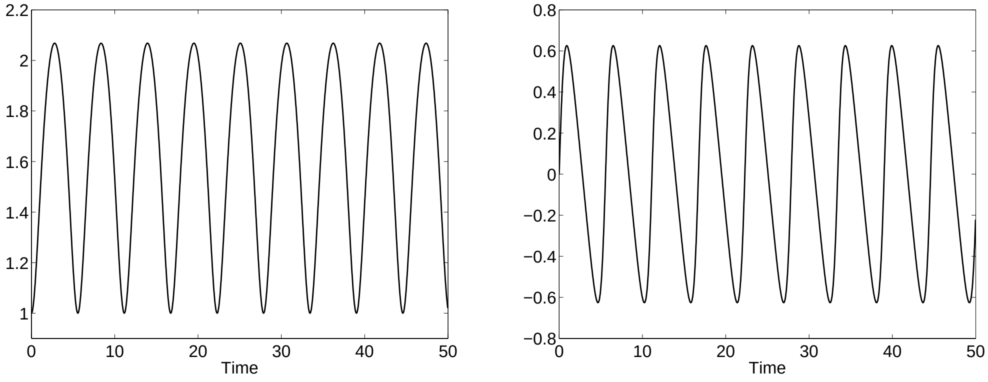
TABLE 1. Maximum relative errors for different values of (N, M) for the hydrogen molecule example.

the existing methods, in particular for problems with moving nuclei (this section) and problems that are periodic (the solid state models considered in the next section).

N	M	Online time for $\partial s_{N,M}(\mu)/\partial\mu$	(Online) time for $\partial s(\mu)/\partial\mu$
2	2	1.26 E − 05	1
4	4	3.98 E − 05	1
6	6	8.07 E − 05	1
8	8	1.18 E − 04	1
10	10	1.82 E − 04	1
12	12	2.44 E − 04	1

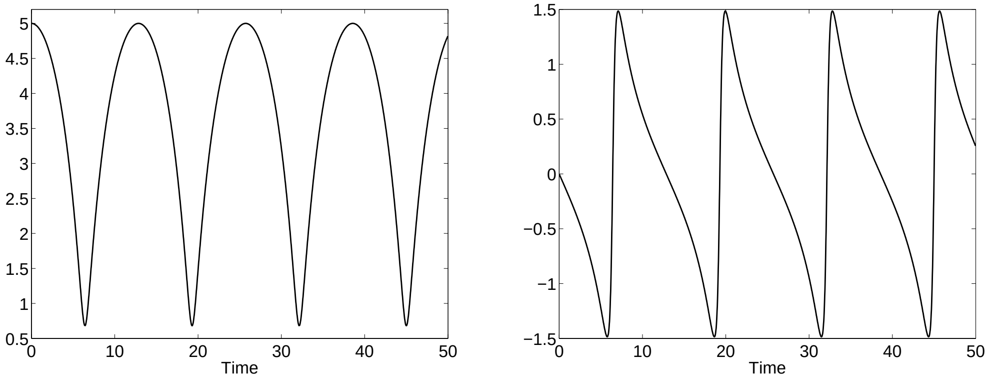
TABLE 2. Online computational times (normalized with respect to the time to solve for $\partial s(\mu)/\partial\mu$) for the hydrogen molecule example.

Finally, we apply our reduced-basis approximation to the real-time molecular dynamics (MD) simulation of the hydrogen molecular system by using the velocity Verlet time integration scheme [**10, 19, 17**]. We present the time evolution of the internuclear separation and velocity in Figure 6 for small initial distance $R_0 = 1.0$ near the equilibrium internuclear separation and in Figure 7 for large initial distance $R_0 = 5.0$ far from the equilibrium internuclear separation. In both cases, we take $N = M = 10$ and use a constant timestep of 0.02 for 2500 time steps. We see that in the first case the two nuclei interact with higher frequency and smaller magnitude than in the second case; and that in the first case the response is relatively harmonic whereas anharmonic effects dominate in the second case. The crucial new ingredient is fast output evaluations that allow us to perform a real-time MD simulation of the hydrogen molecular system: the "ab initio" molecular dynamics results are obtained online in less than 53 seconds on a Pentium 1.73 GHz laptop. (The same simulation would take 73 hours with the (admittedly sub-optimal) FE approximation.)



(a) (b)

FIGURE 6. MD simulation of the H_2 system for $R_0 = 1.0$: (a) internuclear separation and (b) velocity.



(a) (b)

FIGURE 7. MD simulation of the H_2 system for $R_0 = 5.0$: (a) internuclear separation and (b) velocity.

4. 1-D Kohn Sham Equation

4.1. Problem Formulation. We shall now consider a one-dimensional periodic quantum problem[4]: we determine the ground state energy of a model periodic system with lattice parameter μ and hence unit cell $\Omega_{\rm o}(\mu) \equiv] - \frac{\mu}{2}, \frac{\mu}{2}]$ based on the spinless Density Functional Theory [**6, 8, 25, 22**]. We further assume that a single nucleus of charge Z lies at the center of the cell and the number of electrons per nucleus is n_e, with $n_e = Z$ for charge neutrality. This model is rudimentary in the understanding of crystalline solids and has been studied in [**31**] and more recently [**5**].

This problem offers several opportunities for us to exercise the methodology described in previous sections: the parameterization procedure allows for efficient implementation of the *online-offline* computational framework; the empirical interpolation procedure allows for coefficient function approximation of the nonlinear terms; and the reduced-basis procedure enables significant reduction in model size and computational cost in the *online* stage. More importantly, this problem introduces the computational challenges imposed by multiple electrons, and allows us to introduce in Section 4.2 a new ingredient that enables us to construct an efficient reduced-basis space and ultimately a smaller reduced-basis problem.

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[4] For a more general treatment of 3-D periodic quantum systems, work is currently being pursued to exploit existing planewave codes [**11**] to efficiently construct the reduced-basis spaces [**26**].

For simplicity, the parameter space consists of μ only; each new Z constitutes a new problem in our reduced-basis approximation. Some possible applications from studying a system with varying μ includes the determination of forces exerted on the nuclei when the structure is deformed, and the characterization of the nonlinear behavior of the elasticity constant.

4.1.1. *Energy Statement.* The equilibrium ground state energy of the above model can be obtained by solving a minimization problem for $\hat{\mathbf{u}}_{\text{o}}([Z,\mu^*]) \equiv (u_{\text{o}\,1},\dots,u_{\text{o}\,n_e})$, where [**3, 7, 18, 17**]

$$\hat{\mathbf{u}}_{\text{o}}([Z,\mu]) = \arg\inf_{\hat{\mathbf{w}}_{\text{o}}} \Big\{ E_{\text{o}}(\hat{\mathbf{w}}_{\text{o}} \equiv (w_{\text{o}\,1},\dots,w_{\text{o}\,n_e}); [Z,\mu]), w_{\text{o},i} \in Y_{\text{o}}, \int_{\Omega_{\text{o}}(\mu)} w_{\text{o}\,i} w_{\text{o}\,j} = \delta_{ij}, 1 \le i,j \le n_e \Big\}, \tag{4.1}$$

$$\mu^*(Z) = \arg\inf_{\mu} \big\{ \mathcal{E}_{\text{o}}(\hat{\mathbf{u}}_{\text{o}}([Z,\mu]); [Z,\mu]); \mu > 0 \big\}; \tag{4.2}$$

here $Y_{\text{o}} \equiv H^1_{\text{per}}(\Omega_{\text{o}}(\mu))$ is the space of μ-periodic functions in $H^1(\mathbb{R})$; $\delta_{ij} = \{1 \text{ if } i = j,\ 0 \text{ otherwise}\}$; and $u_{\text{o}\,i}$ is the Kohn-Sham orbital associated with the ith electron. (In practice, as in previous sections, Y_{o} is in fact our "truth" approximation, in this case a linear finite element approximation; a planewave (Fourier spectral) "truth" approximation is also possible.) The electronic energy $E_{\text{o}}(\hat{\mathbf{w}}_{\text{o}};[Z,\mu])$ is defined as

$$\begin{aligned} E_{\text{o}}(\hat{\mathbf{w}}_{\text{o}};[Z,\mu]) = {} & C_w \sum_{i=1}^{n_e} \int_{\Omega_{\text{o}}(\mu)} (\nabla w_{\text{o}\,i})^2 - \ Z \sum_{i=1}^{n_e} \int_{\Omega_{\text{o}}(\mu)} G_{\text{o}}\ {w_{\text{o}\,i}}^2 \\ & + \frac{1}{2} C_c \int_{\Omega_{\text{o}}(\mu)} \int_{\Omega_{\text{o}}(\mu)} \left(\sum_{i=1}^{n_e} w^2_{\text{o}\,i}(y_1) \right) \ G_{\text{o}}(y_1 - y_2) \ \left(\sum_{j=1}^{n_e} w^2_{\text{o}\,j}(y_2) \right) \ dy_1\ dy_2 \\ & - C_x \sum_{i=1}^{n_e} \int_{\Omega_{\text{o}}(\mu)} \left(\sum_{j=1}^{n_e} w^2_{\text{o}\,j} \right)^{4/3} w^2_{\text{o}\,i}, \end{aligned} \tag{4.3}$$

where we have used the X-α approximation to approximate the exchange-correlation term. Here, y denotes a point in $\Omega_{\text{o}}(\mu)$; C_w, C_c, and C_x are model constants (currently $C_w = 0.5$, $C_c = 1$ and $C_x = 0.7386$); and the periodic Green's function $G_{\text{o}}(\cdot\,;\mu)\colon\ \Omega_{\text{o}}(\mu) \to \mathbb{R}$ satisfies $-\triangle G_{\text{o}} = \left\{ \delta(y) - \frac{1}{|\Omega_{\text{o}}(\mu)|} \right\}, \int_{\Omega_{\text{o}}(\mu)} G_{\text{o}} = 0$, where $\triangle$ is the Laplacian operator, $\delta(y)$ is the Dirac delta distribution, and $|\Omega_{\text{o}}(\mu)| = \mu$ is the length of $\Omega_{\text{o}}(\mu)$. The total energy $\mathcal{E}_{\text{o}}(\hat{\mathbf{w}}_{\text{o}};[Z,\mu])$ — our output of interest — is then given by

$$\mathcal{E}_{\text{o}}(\hat{\mathbf{w}}_{\text{o}};[Z,\mu]) = E_{\text{o}}(\hat{\mathbf{w}}_{\text{o}};[Z,\mu]) + \frac{Z^2}{2}\eta, \tag{4.4}$$

where η is the nuclear - nuclear correction term given by $\eta = \lim_{y\to 0} \left\{ G_{\text{o}}(y;\mu) - \frac{|y|}{2} \right\} = \frac{\pi^2\mu}{12}$.

Finally, the equivalent Euler-Lagrange equations for the constrained minimization problem (4.1) is given by:

$$C_w \Delta u_{\text{o}\,i} - G_{\text{o}} u_{\text{o}\,i} - \phi_{\text{o}} u_{\text{o}\,i} + C_x \left(\sum_{j=1}^{n_e} u^2_{\text{o}\,j} \right)^{1/3} u_{\text{o}\,i} = \lambda_{\text{o}\,i} u_{\text{o}\,i}, \qquad 1 \le i \le n_e, \tag{4.5}$$

$$-\Delta\phi_{\text{o}} - 4\pi C_c \left[\frac{Z}{\Omega_{\text{o}}(\mu)} - \sum_{j=1}^{n_e} u^2_{\text{o}\,j} \right] = 0, \tag{4.6}$$

$$\int_{\Omega_{\text{o}}(\mu)} u_{\text{o}\,i} u_{\text{o}\,j} = \delta_{ij}, \qquad 1 \le i < j < n_e \tag{4.7}$$

$$\int_{\Omega_{\text{o}}(\mu)} \phi_{\text{o}} = 0. \tag{4.8}$$

Here, $\phi_{\rm o} = -C_c \int_{\Omega_{\rm o}(\mu)} \left(\sum_{j=1}^{n_e} u_{{\rm o}\,j}^2 \right) G_{\rm o}(y_1 - y_2) dy_2$ is simply the Hartree potential [**7**] with a normalization of $\int_{\Omega_{\rm o}(\mu)} \phi_{\rm o} = 0$. Note that (4.5) contains a nonlinear term similar to Section 2.3; but now we have an eigenvalue problem for which we need to determine n_e eigenfunctions (or orbitals) and eigenvalues.

4.1.2. *Parameterized Abstract Formulation.* From the weak form of the Euler Lagrange equations (4.5) - (4.8), we derive the equivalent parameterized abstract formulation. We first define an affine geometric mapping, $\mathcal{G}(\mu)$, from $\Omega_{\rm o}(\mu)$ to $\Omega \equiv]-\frac{1}{2}, \frac{1}{2}]$, which can be expressed as $x = \mathcal{G}(y;\mu) \equiv \frac{1}{\mu} y$. We further define $u_i(\mu) = u_{{\rm o}\,i} \circ \mathcal{G}^{-1}(\,\cdot\,;\mu)$, $\phi(\mu) = \frac{1}{\mu}\phi_{\rm o} \circ \mathcal{G}^{-1}(\,\cdot\,;\mu)$ and $G(\mu) = \frac{1}{\mu} G_{\rm o} \circ \mathcal{G}^{-1}(\,\cdot\,;\mu)$. Then, $\mathbf{u}([Z,\mu]) \equiv (\hat{\mathbf{u}}([Z,\mu])$, $\phi([Z,\mu])$, $\hat{\lambda}([Z,\mu])$, $\tau([Z,\mu])) \in \mathcal{Y} \equiv ((Y)^{n_e} \times Y \times \mathbb{R}^{n_e(n_e+1)/2} \times \mathbb{R})$ satisfies

$$\mathcal{A}(\mathbf{u}([Z,\mu]), \mathbf{v}; G; [Z,\mu]) = 0, \qquad \forall \mathbf{v} \in \mathcal{Y}, \tag{4.9}$$

where $Y \equiv H^1_{\rm per}(\Omega)$ is the space of 1-periodic functions in $H^1(\mathbb{R})$ (more precisely, an associated "truth" approximation subspace) with the associated inner product $(w,v)_Y \equiv \int_\Omega \nabla w \cdot \nabla v + \int_\Omega wv$ and norm $||\cdot|| = (\cdot,\cdot)_Y^{1/2}$; $\hat{\mathbf{u}}([Z,\mu]) \equiv (u_i, 1 \le i \le n_e)$; $\hat{\lambda}([Z,\mu]) \equiv (\lambda_{ij}, 1 \le i \le j \le n_e)$; G satisfies $-\Delta G = \delta(x) - 1$, $\int_\Omega G = 0$; and $\mathcal{A}$ is defined as

$$\begin{aligned}
&\mathcal{A}(\mathbf{w} \equiv (\hat{\mathbf{w}}, s, \hat{\sigma}, \kappa), \mathbf{v} \equiv (\hat{\mathbf{v}}, \varsigma, \hat{\varphi}, \varpi); t; [Z,\mu]) \equiv \\
&\qquad \sum_{i=1}^{n_e} \Bigg[\theta_1\ a_0(w_i, v_i) + \ \theta_2\ a_2(w_i, t, v_i) + \theta_3\ a_2(w_i, s, v_i) + \theta_5\ a^{\rm nl}(w_i, \sum_{j=1}^{n_e} w_j^2, v_i) \\
&\qquad + \theta_4\ \sigma_{ii} a_1(u_i, v_i) + \theta_4\ \sum_{j=1}^{n_e} \sigma_{ij}\ a_1(w_j, v_i) \Bigg] + \sum_{i=1}^{n_e} \sum_{j=i}^{n_e} \varphi_{ij} \left\{ \beta_1 a_1(w_i, w_j) + \beta_2 \delta_{ij} \right\} + \\
&\qquad \left[\alpha_1 a_0(s, \varsigma) + \alpha_2 \sum_{j=1}^{n_e} a_2(w_j, w_j, \varsigma) + \alpha_3 l(\varsigma) + \kappa \alpha_4\ l(\varsigma) \right] + \varpi\ l(s).
\end{aligned} \tag{4.10}$$

Here, $a_0(w,v) \equiv \int_\Omega \nabla w \nabla v$, $a_1(w,v) \equiv \int_\Omega wv$, $a_2(w,s,v) \equiv \int_\Omega wsv$, $a^{\rm nl}(w,t,v) \equiv \int_\Omega w t^{1/3} v$, and $l(w) \equiv \int_\Omega w$ for any $w \in Y$, $v \in Y$, $s \in Y$, and non-negative $t \in Y$. For prescribed C_w, C_x, and C_c[5] $\theta(Z,\mu) = \left\{ \frac{C_w}{\mu}, -Z\mu^2, -\mu^2, -\frac{\mu}{2}, -C_x \frac{4}{3}\mu \right\}$, $\alpha(Z,\mu) = \{1, C_c\mu, -C_c Z, \mu\}$ and $\beta(Z,\mu) = \{\mu, -1\}$.

The total energy $\mathcal{E}(\mathbf{u}([Z,\mu]); G; [Z,\mu])$ is then given by

$$\begin{aligned}
\mathcal{E}(\mathbf{w} \equiv (\hat{\mathbf{w}}, s, \hat{\sigma}, \kappa); G; [Z,\mu]) \ &= \ \sum_{i=1}^{n_e} [\theta_1 a_0(w_i, w_i) + \theta_2\ a_2(w_i, G, w_i) \\
&\quad + \frac{1}{2}\theta_3\ a_2(w_i, s, w_i) + \frac{3}{4}\theta_5\ a_1^{\rm nl}(w_i, \sum_{j=1}^{n_e} w_j^2, w_i)] + \frac{Z^2}{2}\eta,
\end{aligned} \tag{4.11}$$

for $\eta = \frac{\pi^2 \mu}{12}$ as defined earlier.

4.2. Reduced-Basis Formulation.

4.2.1. *Reduced-Basis Spaces.* Proceeding from Sections 2.2 and 3.2, it is not immediately clear how we should construct our reduced-basis space for this multi-electron problem — there are now n_e components to the solution. A simplest (and perhaps naive) approach would be as follows: we introduce nested sample sets $S^u_{N^u_{\rm naive}} = \{\mu^u_1, \ldots, \mu^u_{N^u_{\rm naive}}\}, 1 \le N^u_{\rm naive} \le N^u_{\rm naive\,max}$; the reduced-basis space is then given by $W^{u,{\rm naive}}_{n_e \times N^u_{\rm naive}} = \text{span}\ \{u_i([Z,\mu^u_n]), 1 \le i \le n_e, 1 \le n \le N^u_{\rm naive}\}$, $1 \le N^u_{\rm naive} \le N^u_{\rm naive\,max}$. For any μ, we now find an approximation to $u_i([Z,\mu])$, $1 \le i \le n_e$, in $W^{u,{\rm naive}}_{n_e \times N^u_{\rm naive}}$. The space $W^{u,{\rm naive}}_{n_e \times N^u_{\rm naive}}$ is sufficiently rich that the approximation will be good, and it provides sufficient degrees of freedom to honor the orthonormality constraints. However, the number of basis functions required is $N^u_{\rm naive} \times n_e$; the size of our problem will increase linearly with n_e and, depending on $N^u_{\rm naive}$, it can rapidly become unacceptably large. In addition, degeneracy can also become an issue.

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[5] For our numerical results, we have used $C_w = 0.5$, $C_x = 0.7386$ and $C_c = 1$.

This bring us to the final ingredient in our method, the vector reduced-basis space. This approximation attempts to exploit (through the reduced basis space) the inherent orthogonality properties between, and the common smoothness of the solutions $u_i([Z,\mu])$, $1 \le i \le n_e$ for a given μ: we introduce nested sample sets $S^u_{N^u} = \{\mu^u_1, \ldots, \mu^u_{N^u}\}, 1 \le N^u \le N^u_{\max}$ and define the associated nested reduced-basis spaces as

$$W^u_{N^u} = \text{span}\ \{\hat{\mathbf{u}}([Z,\mu^u_n]), 1 \le n \le N^u\}, \quad 1 \le N^u \le N^u_{\max}, \tag{4.12}$$

$$= \text{span}\ \{\hat{\zeta}_n, 1 \le n \le N^u\}, \quad 1 \le N^u \le N^u_{\max}; \tag{4.13}$$

where $\hat{\mathbf{u}}([Z,\mu^u_n]) \equiv (u_1([Z,\mu^u_n]), \ldots, u_{n_e}([Z,\mu^u_n]))$ are the solutions of (4.10) at $\mu = \mu^u_n$ for a given Z; and $\hat{\zeta} \equiv (\zeta_1, \ldots, \zeta_{n_e})$ are basis functions obtained after $\hat{\mathbf{u}}([Z,\mu^u_n]), 1 \le n \le N^u$ are aligned and pseudo-orthogonalized; these two preprocessing steps will lead to smaller N^u and better stability in the resulting discrete system, and will be described in the following paragraphs. Then, an approximation of $\hat{\mathbf{u}}$ in W^u_N is given by $\hat{\mathbf{u}}_{N,M}(\mu) = \sum_{n=1}^{N^u} \psi_n(\mu)\hat{\zeta}_n$ — the ith component of $\hat{\mathbf{u}}_{N,M}(\mu)$ is given by $u_{N,M\ i}(\mu) = \sum_{n=1}^{N^u} \psi_n(\mu)(\zeta_i)_n$, $1 \le i \le n_e$.

We shall now describe the preprocessing steps alluded to earlier. First, we observe that the solutions $\hat{\mathbf{u}}$ obtained based on a numerical algorithm such as the Arnoldi Method [**32**] are usually presented in ascending order of their respective eigenvalues, λ_{ii}, and not according to any particular structure of the orbitals identified by the form of the solutions $u_i([Z,\mu])$, $1 \le i \le n_e$. This, in addition to fact that the orbitals are only equivalent up to a sign, leads to discontinuities in $u_i([Z,\mu])$, $1 \le i \le n_e$ in the parameter space, as shown in Figure 8. Referring to Figure 8, we can identify three types of discontinuities: (1) sign switching (as demonstrated by u_1, u_4, and u_5); (2) mode crossing, where u_2 at $\mu = 4.5$ and 5.5 are a smooth transition of u_3 at $\mu = 1.5$, 2.5 and 3.5, and vice versa; and (3) mode entering, where there are more than n_e forms of orbitals appearing in our solutions as μ varies (not exhibited by the solutions in Figure 8).

The alignment process seeks to remove the first two discontinuities by employing the following greedy algorithm: given a pre-sorted space $W^u_{N^u} \equiv \text{span}\ \{\hat{\zeta}^s_n, 1 \le n \le N^u\}$ where $\hat{\zeta}^s_n$, $1 \le n \le N^u$ are the sorted basis functions of $\hat{\mathbf{u}}_n$, $1 \le n \le N^u$, we wish to add $\hat{\mathbf{u}}([Z,\mu^u_{N^u+1}])$ to $W^u_{N^u}$ to form $W^u_{N^u+1}$. We first select a $\hat{\zeta}^s_n \in W^u_{N^u}$ such that $\mu^u_n \in S^u_{N^u}$ is closest to $\mu^u_{N^u+1}$. We compute $e^+_{w,j} = ||(\zeta^s_1)_n + u_j(\mu^u_{N^u+1})||_Y$ and $e^-_{w,j} = ||(\zeta^s_1)_n - u_j(\mu^u_{N^u+1})||_Y$ for $1 \le j \le n_e$; we then determine $j^* \equiv \arg\min_{j, 1 \le j \le n_e}\{e^+_{w,j}, e^-_{w,j}\}$. If $e^-_{w,j^*} > e^+_{w,j^*}$, then $(\zeta^s_1)_{N^u+1} = -u_{j^*}(\mu^u_{N^u+1})$; otherwise $(\zeta^s_1)_{N^u+1} = u_{j^*}(\mu^u_{N^u+1})$. This is then repeated for all $(\zeta^s_i)_{N^u+1}$, for $i = 2, \ldots, n_e$. First part of the algorithm associates $u_j(\mu)$ to the correct orbital and the second part of the algorithm remove the sign variation in ζ^s_i. The results are sets of orbitals that vary smoothly with μ, as shown in Figure 9.[6]

The sorted bases are then pseudo-orthogonalized: given a space $W^u_{N^u} = \text{span}\ \{\hat{\zeta}_n, 1 \le n \le N^u\}$ where $\hat{\zeta}_n$ are the pseudo-orthogonalized basis functions of $\hat{\zeta}^s_n$, $1 \le n \le N^u$, and the next member of the space, $\hat{\zeta}^s([Z,\mu^u_{n+1}])$, we first compute $\hat{\mathbf{b}} = \hat{\zeta}^s - \sum_{n=1}^{N^u} \nu_n \hat{\zeta}_n$, where $\nu = \arg\min_{\nu \in \mathbb{R}^{N^u}} \sum_{i=1}^{n_e} ||\zeta^s_i - \sum_{n=1}^{N^u} \nu_n (\zeta_i)_n||^2_Y$; the new basis, pseudo-orthogonalized, is then given by $\hat{\zeta}_{N^u+1} = \hat{\mathbf{b}}/(\frac{1}{n_e}\sum_{i=1}^{n_e} ||b_i||^2_Y)^{1/2}$ and $W^u_{N^u+1} = W^u_{N^u} + \hat{\zeta}_{N^u+1}$.

We may similarly define for ϕ the nested sample sets $S^\phi_{N^\phi} = \{\mu^\phi_1, \ldots, \mu^\phi_{N^\phi}\}$ and the associated reduced-basis space $W^\phi_{N^\phi} = \text{span}\ \{\phi([Z,\mu^\phi_n]), 1 \le n \le N^\phi\} = \text{span}\ \{\chi_n, 1 \le n \le N^\phi\}$, $1 \le N^\phi \le N^\phi_{\max}$. The χ_n, $1 \le n \le N^\phi$ are obtained by orthonormalizing $\phi([Z,\mu^\phi_n])$, $1 \le n \le N^\phi$ relative to the $(\cdot;\cdot)_Y$ inner product.

Finally (although in actual practice, initially), we construct the $S^u_{N^u}$ and $S^\phi_{N^\phi}$ based on the greedy selection process. As described in Section 2.2.1, we may employ different forms of error measures. Here, we first construct $S^\phi_{N^\phi}$ (and correspondingly $W^\phi_{N^\phi}$) based on the greedy selection process using the projection error as defined by (2.12); we wish to isolate the behavior of the space $W^u_{N^u}$. The $S^u_{N^u}$ (and correspondingly $W^u_{N^u}$) is then constructed based on the greedy selection process using the reduced-basis error defined as $\frac{(\sum_{i=1}^{n_e} ||u_i([Z,\mu]) - u_{N,M\ i}([Z,\mu])||^2_Y)^{1/2}}{(\sum_{i=1}^{n_e} ||u_i([Z,\mu])||^2_Y)^{1/2}}$. The approximations by which $\hat{\mathbf{u}}_{N,M}([Z,\mu])$ are obtained will now be elaborated.

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[6] The 3rd type of the discountinuities — mode entering — has to be handled differently. We may allow this discontinuity to exist although the resulting approximation is sub-optimal. Alternatively, one could expand the number of orbitals taken into account, i.e. we may wish to construct a reduced-basis space given by $W^{u,\text{augment}}_{N^u} \equiv \text{span}\ \{\hat{\mathbf{u}}([Z,\mu^u_n]) \equiv (u_1([Z,\mu^u_n]), \ldots, u_{n_{e,\text{augment}}}([Z,\mu^u_n])),\ 1 \le n \le N^u\}$, where $n_{e,\text{augment}} > n_e$ and $n_{e,\text{augment}}$ is sufficiently large such that the discontinuity resulting from mode entering does not appear within our parameter space of interest. Thanks to the vectorial nature of $W^{u,\text{augment}}_{N^u}$, this will not lead to significant increase in the N^u required.

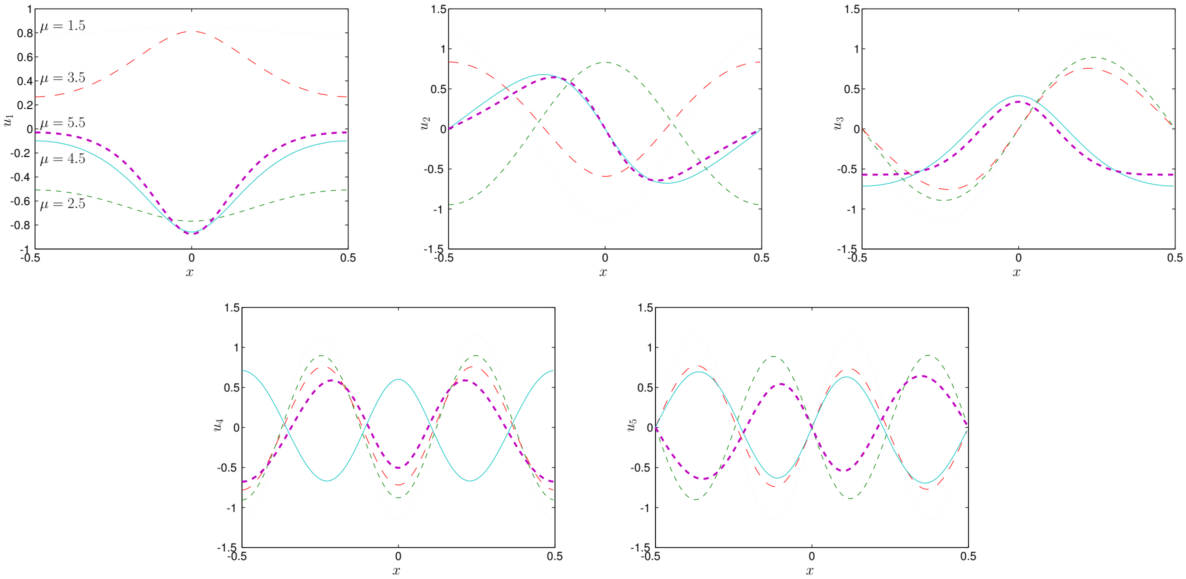

FIGURE 8. Solutions of $\hat{\mathbf{u}}(\mu)$ at $\mu = 1.5, 2.5, 3.5, 4.5$ and 5.5, before the alignment process.

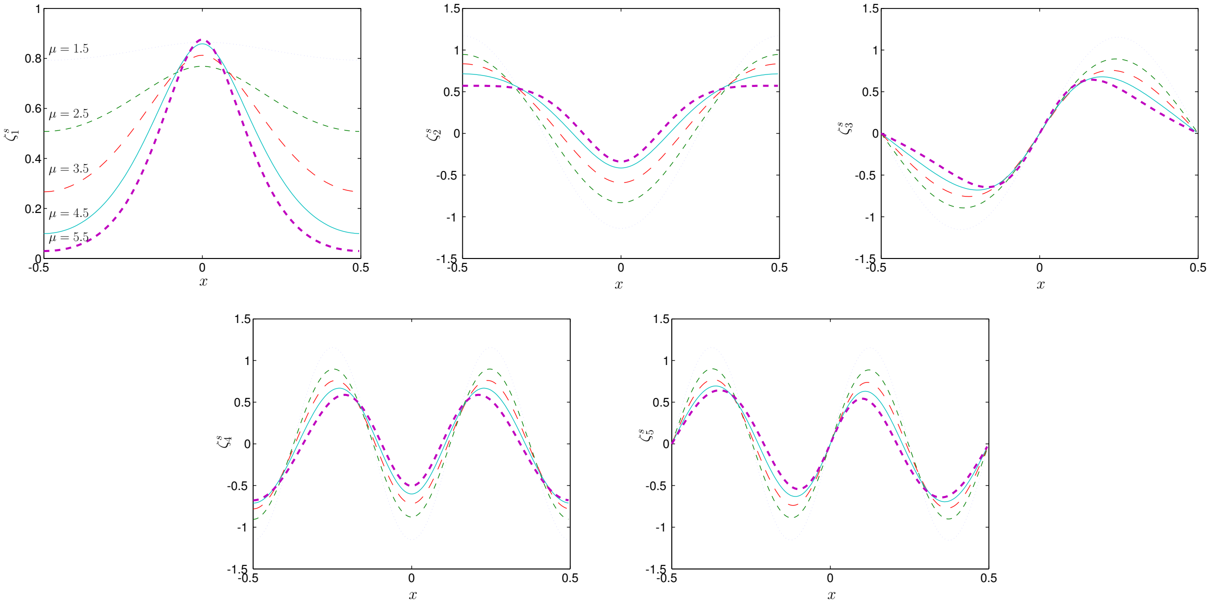

FIGURE 9. $\hat{\zeta}^s$ at $\mu = 1.5, 2.5, 3.5, 4.5$ and 5.5, after the alignment process.

4.2.2. *The Approximations.* In our reduced-basis approximation, the equilibrium ground state of the resulting neutral structure for a particular $Z\ (= n_e)$ is given by $\hat{\mathbf{u}}_{N,M}([Z,\mu]) \equiv (u_{N,M\,1}([Z,\mu]), \ldots, u_{N,M\,n_e}([Z,\mu]))$, where

$$\hat{\mathbf{u}}_{N,M}([Z,\mu]) \quad = \quad \arg\inf_{\hat{\mathbf{w}}} \Big\{ E_{N,M}(\hat{\mathbf{w}} \equiv (w_1, \ldots, w_{n_e}); [Z,\mu]), w_i \in W_N^u, \mu \int_\Omega w_i^2 = 1, 1 \le i \le n_e \Big\}, \tag{4.14}$$

$$\mu^*(Z) \quad = \quad \arg\inf_{\mu} \{ \mathcal{E}_{N,M}(\hat{\mathbf{u}}_{N,M}([Z,\mu]); [Z,\mu]); \mu > 0 \}. \tag{4.15}$$

Here, $\hat{\mathbf{u}}_{N,M}([Z,\mu])$ is obtained by solving the following Euler Lagrange equations: find $\mathbf{u}_{N,M}([Z,\mu]) \equiv (\hat{\mathbf{u}}_{N,M}([Z,\mu]),\ \phi_{N,M}([Z,\mu]),\ \hat{\lambda}_{N,M}([Z,\mu]),\ \tau_{N,M}([Z,\mu])) \in \mathcal{Y}_N \equiv (W^u_{N^u} \times W^\phi_N \times \mathbb{R}^{n_e} \times \mathbb{R})$ such that

$$\mathcal{A}_M(\mathbf{u}_{N,M}([Z,\mu]), \mathbf{v}; G; [Z,\mu]) = 0, \qquad \forall \mathbf{v} \equiv (\hat{\mathbf{v}}, \varsigma, \hat{\varphi}, \varpi) \in \mathcal{Y}_N, \tag{4.16}$$

where $\hat{\lambda}_{N,M}([Z,\mu]) \equiv ((\lambda_{N,M})_{ii}, 1 \le i \le n_e)$ and

$$\begin{aligned}
&\mathcal{A}_M(\mathbf{w} \equiv (\hat{\mathbf{w}}, s, \hat{\sigma}, \kappa), \mathbf{v} \equiv (\hat{\mathbf{v}}, \varsigma, \hat{\varphi}, \varpi); t; [Z,\mu]) \equiv \\
&\quad \sum_{i=1}^{n_e} \Bigg[\theta_1\ a_0(w_i, v_i) +\ \theta_2\ a_2(w_i, t, v_i) + \theta_3\ a_2(w_i, s, v_i) + \theta_5\ a^{\mathrm{nl,M}}(w_i, \sum_{j=1}^{n_e} w_j^2, v_i) \\
&\quad + 2\theta_4\ \sigma_{ii} a_1(w_i, v_i)] + \sum_{i=1}^{n_e} \varphi_{ii} \left\{\beta_1 a_1(w_i, w_i) + \beta_2 \delta_{ii}\right\} + \\
&\quad \left[\alpha_1 a_0(s, \varsigma) + \alpha_2 \sum_{j=1}^{n_e} a_2(w_j, w_j, \varsigma) + \alpha_3 l(\varsigma) + \kappa\alpha_4\ l(\varsigma)\right] + \varpi\ l(s).
\end{aligned}$$

Then, $E_{N,M}(\mathbf{u}_{N,M}([Z,\mu]); G; [Z,\mu])$, the reduced-basis approximation for the electronic energy $E(\mathbf{u}([Z,\mu]); G; [Z,\mu])$, is given by

$$\begin{aligned}
E_{N,M}(\mathbf{w} \equiv (\hat{\mathbf{w}}, s, \hat{\sigma}, \kappa); G; [Z,\mu]) &= \sum_{i=1}^{n_e} [\theta_1 a_0(w_i, w_i) +\ \theta_2\ a_2(w_i, G, w_i) + \frac{1}{2}\theta_3\ a_2(w_i, s, w_i) \\
&\quad + \frac{3}{4}\theta_5\ a^{\mathrm{nl,M}}(w_i, \sum_{j=1}^{n_e} w_j^2, w_i)].
\end{aligned} \tag{4.17}$$

and $\mathcal{E}_{N,M}(\mathbf{u}_{N,M}([Z,\mu]); G; [Z,\mu])$, the reduced-basis approximation to the total energy $\mathcal{E}(\mathbf{u}([Z,\mu]); G; [Z,\mu])$, is given by $E_{N,M}(\mathbf{u}_{N,M}([Z,\mu]); G; [Z,\mu]) + \frac{Z^2}{2}\eta(\mu)$.

When compared to (4.1) and (4.10), we have made two approximations. First, we approximate $a^{\mathrm{nl}}(w_i, \sum_{j=1}^{n_e} w_j^2, v_i)$ by $a^{\mathrm{nl,M}}(w_i, \sum_{j=1}^{n_e} w_j^2, v_i) \equiv \int_\Omega g^w_{M\ i}\ v$, where $g^u_{M\ i}$ is an empirical interpolation approximation to $g_i(\hat{\mathbf{u}}) \equiv u_i(\sum_{j=1}^{n_e} u_j^2)^{1/3}$. Thus, we require n_e empirical interpolation approximations. Secondly, we only impose the constraints $\mu \int_\Omega u^2_{N,M\ i} = 1, 1 \le i \le n_e$. Note that in the original minimization problem (4.9), the constraints are $\mu \int_\Omega u_i u_j = \delta_{ij}, 1 \le i < j \le n_e$; we have thus assumed that the orthogonality of the components in $\hat{\mathbf{u}}_{N,M}$ will be approximately satisfied by construction (implicit to our space $W^u_{N^u}$) in (4.16). We note that $\int_\Omega u_{N,M\ i}\ u_{N,M\ j}$, $1 \le i < j \le n_e$ can be bounded: let $(w,v)_{L^2} = a_1(w,v) = \int_\Omega wv$ and $||\cdot||_{L^2} = \sqrt{(\cdot,\cdot)_{L^2}}$; then

$$\begin{aligned}
(u_{N,M\ i}, u_{N,M\ j})_{L^2} &= (u_{N,M\ i} - u_i, u_{N,M\ j})_{L^2} + (u_i, u_{N,M\ j} - u_j)_{L^2} + (u_i, u_j)_{L^2} \\
&\le ||u_{N,M\ i} - u_i||_{L^2} + ||u_{N,M\ j} - u_j||_{L^2},
\end{aligned} \tag{4.18}$$

since $||u_i||_{L^2} = ||u_{N,M\ j}||_{L^2} = 1$ and $(u_i, u_j)_{L^2} = 0$, for all $1 \le i < j \le n_e$. Therefore,

$$(u_{N,M\ i}, u_{N,M\ j})_{L^2} \le \sum_{n=1}^{n_e} ||u_n - u_{N,M\ n}||_{L^2}. \tag{4.19}$$

From above, we can conclude that as $\hat{\mathbf{u}}_{N,M} \to \hat{\mathbf{u}}$, $\int_\Omega u_{N,M\ i}\, u_{N,M\ j} \to 0$, for $1 \le i < j \le n_e$.

However, note that for N^u sufficiently large, we can represent any member of our (finite-dimensional) truth approximation space, presuming the linear indepedence of the snapshots. But, clearly (4.14) is not equivalent to (4.1) due to the absence of the orthogonality constraints. Hence, to be consistent, as N^u increases, we should also systematically add in orthogonality constraints, for example by adding one orthogonality constraint for every two additional basis functions. This will be considered in future work.

Finally, since $\int_\Omega \chi_n = 0$, $1 \le n \le N$, $\int_\Omega \phi_{N,M}$ is perforce zero; our discrete (nonlinear) algebraic system will thus have an actual dimension of $N^u + N^\phi + n_e$.

4.2.3. *Solution Method.* Our truth approximations are obtained based on the finite element formulation with $\mathcal{N} = 400$. The resulting discrete equation is solve through self-consistent field procedure [**6, 4**]: the nonlinearity is tackled based on a fixed point method in which a diagonalization of the algebraic system for (4.10) is performed within each iteration. As shown in Figure 9, the solutions in $\hat{\mathbf{u}}$ exhibit considerable variation with respect to μ.

However, the fixed point method is not suited for our reduced-basis approximation given by (4.16). We thus resort to Newton's method as described in Section 2.2.2, and, to assist convergence, we exploit a homotopy procedure in $\epsilon \in [0,1]$ and $\mu_k = \mu_i + \epsilon(\mu - \mu_i)$, where μ_k is the μ at k intermediate homotopy step and μ_i is the initial $\mu_{k=0}$ at start of the homotopy procedure — usually chosen to be the closest $\mu^u \in S^u_{N^u}$ to μ. The online complexity is then $O((N^\phi)^3 + n_e N^\phi (N^u)^2 + (N^u)^2 + n_e N^u M)$ per Newton iteration.

4.3. Numerical Results. We consider μ in the interval $[1.5, 5.5]$. We introduce a parameter test sample Ξ_{Test} of size 161 and choose M, the dimension of the empirical interpolation space, such that ε_M is less than 10^{-10}. We then define the following

$$\varepsilon^u_{N,M} = \max_{\mu \in \Xi_{\text{Test}}} \frac{(\sum_{i=1}^{n_e} ||u_i([Z,\mu]) - u_{N,M\,i}([Z,\mu])||^2_Y)^{1/2}}{(\sum_{i=1}^{n_e} ||u_i([Z,\mu])||^2_Y)^{1/2}}, \tag{4.20}$$

$$\varepsilon^\phi_{N,M} = \max_{\mu \in \Xi_{\text{Test}}} \frac{||\phi([Z,\mu]) - \phi_{N,M}([Z,\mu])||_Y}{||\phi([Z,\mu])||_Y}, \tag{4.21}$$

$$\varepsilon^{\mathcal{E}}_{N,M} = \max_{\mu \in \Xi_{\text{Test}}} |\mathcal{E}_N([Z,\mu]) - \mathcal{E}([Z,\mu])| / |\mathcal{E}([Z,\mu])| \tag{4.22}$$

$$\varepsilon^{\text{ortho}}_{N,M} = \max_{\mu \in \Xi_{\text{Test}}} \max_{1 \le i < j \le n_e} (u_{N,M\,i}([Z,\mu]), u_{N,M\,j}([Z,\mu]))_{L^2}. \tag{4.23}$$

where $\varepsilon^u_{N,M}$, $\varepsilon^\phi_{N,M}$ and $\varepsilon^{\mathcal{E}}_{N,M}$ are respectively the maximum error in the reduced-basis approximation of $\hat{\mathbf{u}}$, ϕ and $\mathcal{E}$ within a given sample Ξ_{Test}; $\varepsilon^{\text{ortho}}_{N,M}$ is a measure of non-compliance in the orthogonality constraints; and $(w,v)_{L^2} = a_1(w,v) = \int_\Omega wv$. We present the results for the above quantities with increasing N^u for $n_e = 5$ in Table 3. Here, N^ϕ is 5 and M is 12. We observe a monotonic decrease in $\varepsilon^u_{N,M}$, $\varepsilon^\phi_{N,M}$ and $\varepsilon^{\mathcal{E}}_{N,M}$. We only require $N^u = 10$ to reduce $\varepsilon^u_{N,M}$ and $\varepsilon^{\mathcal{E}}_{N,M}$ to 9.76×10^{-6} and 3.05×10^{-10} respectively. In addition, $\varepsilon^{\mathcal{E}}_{N,M}$ is approximately the square of $\varepsilon^u_{N,M}$ (and $\varepsilon^\phi_{N,M}$), indicating that $\mathcal{E}$ can in fact be approximated very accurately with very few basis functions by $\mathcal{E}_{N,M}$; there is virtually no noticeable distinction between the two as shown in figure 10.

From Table 3, we also observe that $\varepsilon^{\text{ortho}}_{N,M}$ converges very rapidly with N^u. This is perhaps not surprising. From (4.19), we obtain

$$\varepsilon^{\text{ortho}}_{N,M} \le \max_{\mu \in \Xi_{\text{Test}}} \sum_{n=1}^{n_e} ||u_n([Z,\mu]) - u_{N,M\,n}([Z,\mu])||_{L^2}. \tag{4.24}$$

This implies that as $\hat{\mathbf{u}}_{N,M}([Z,\mu]) \to \hat{\mathbf{u}}([Z,\mu])$, $\varepsilon^{\text{ortho}}_{N,M} \to 0$ and since $\varepsilon^u_{N,M}$ decreases with increasing N^u, so does $\varepsilon^{\text{ortho}}_{N,M}$ [7]. The error $\varepsilon^{\text{ortho}}_{N,M}$ can certainly be reduced further by the systematic inclusion of orthogonality constraints, as argued in Section 4.2.2.

The above results can be extended to other cases of $n_e > 1$. In Figure 11, we show that the convergence results of the error $\varepsilon^u_{N,M}$ with respect to N^u for $3 \le n_e \le 8$. We observe that the error decreases monotonically with increasing N^u and with just 12 basis functions in $W^u_{N^u}$, an error of $\varepsilon^u_{N,M} < 10^{-5}$ can be obtained for the $n_e = 8$ case. In addition, the number of basis functions required for each case is only slightly higher than n_e; N^u scales approximately as $n_e + C$, where C is a small integer. The naive approach which does not exploit the vectorial nature of the reduced basis space (as described at beginning of Section 4.2.1) will require $N^u_{\text{naive}} \times n_e$ basis functions, and hence is much more sensitive to the number of electrons.

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[7] At $N = n_e$, the apparent "good orthogonality" is deceiving — the size of N is too small and the reduced-basis solution gravitates towards a single basis, of which the orthogonality is obviously satisfied.

N^u	$\varepsilon^u_{N,M}$	$\varepsilon^{\mathcal{E}}_{N,M}$	$\varepsilon^{\phi}_{N,M}$	$\varepsilon^{\text{ortho}}_{N,M}$
5	7.9044 E − 2	4.6557 E − 04	1.4647 E + 0	5.1756 E − 14
6	4.5693 E − 2	3.5279 E − 05	1.2839 E − 1	3.6342 E − 3
7	2.1383 E − 4	1.3947 E − 09	1.0334 E − 3	2.1783 E − 5
8	9.8819 E − 5	8.8168 E − 10	3.7635 E − 4	1.0686 E − 5
9	9.7602 E − 6	3.0509 E − 10	3.8463 E − 5	8.9840 E − 7

TABLE 3. Variations of the reduced-basis errors $\varepsilon^u_{N,M}$, $\varepsilon^{\mathcal{E}}_{N,M}$, $\varepsilon^{\phi}_{N,M}$ and $\varepsilon^{\text{ortho}}_{N,M}$ with N^u. Here, $n_e = 5$ and $1.5 \leq \mu \leq 5.5$.

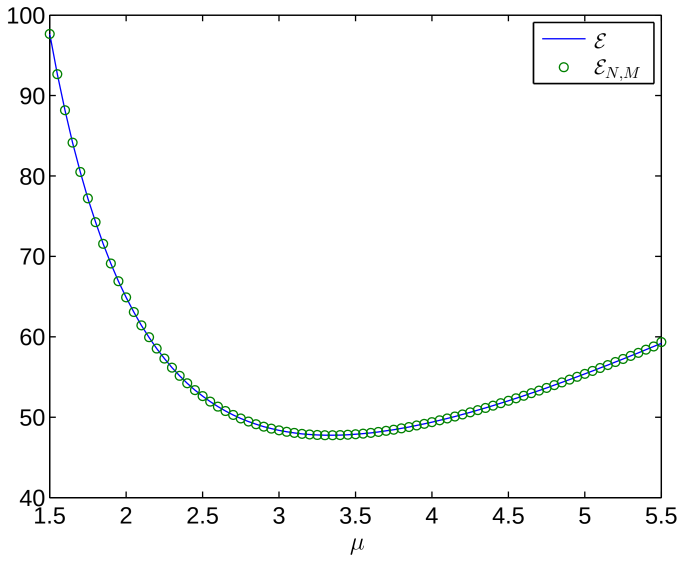

FIGURE 10. Comparison between $\mathcal{E}$ and $\mathcal{E}_{N,M}$ for $n_e = 5$, $1.5 < \mu < 5.5$; there is no discernable difference between the two.

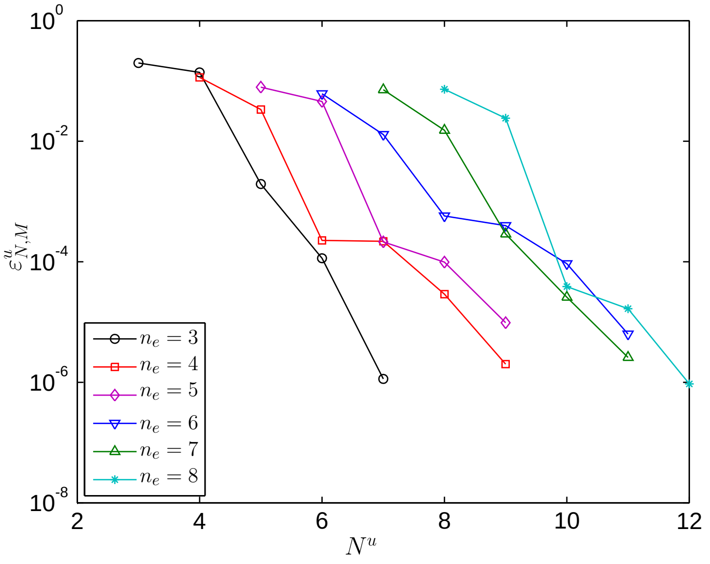

FIGURE 11. Convergence of the reduced basis error $\varepsilon^u_{N,M}$ for $3 \leq n_e \leq 8$. The μ range is $[1.5, 5.5]$.

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